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Investigation of a Honeywell Dissolved Oxygen Parametric System

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April 1977

INVESTIGATION
OF A
HONEYWELL DISSOLVED OXYGEN PARAMETRIC SYSTEM

by

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati conducts research to:

develop and evaluate techniques to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste;

investigate ways to concentrate, recover, and identify viruses, bacteria, and other microbiological organisms in water, and to study the responses of aquatic organisms to water quality; and

assure Agency-wide standardization and quality control of systems used to monitor water and wastewater.

This investigation of the Honeywell submersible model dissolved oxygen parametric system, one of many instrumentation systems investigated by the Instrumentation Development Branch, was pursued to determine the effectiveness of that system in Environmental Protection Agency research sewage treatment programs.

Dwight G. Ballinger
Director
Environmental Monitoring and Support Laboratory
Cincinnati

ABSTRACT

A Honeywell dissolved oxygen parametric system was investigated for possible application in EPA's research on sewage treatment. Laboratory and field data were accumulated. Summaries on selected background and theoretical aspects of the measurement have been included for those unfamiliar with this type of instrumentation.

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[a]Wastewater Research Division, Municipal Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio.

SECTION 1

INTRODUCTION

The basic objective of this study was to determine through laboratory and field investigations whether Honeywell's submersible model dissolved oxygen parametric system,[1] is suitable for use in EPA's programs, especially those involving sewage treatment plants.

Honeywell has been a major supplier of this type of instrumentation and provided this particular system for application and investigation by EPA.

It is evident that an instrument system employed in field applications--whether for permit program, enforcement, regulatory, or for process control--must be ruggedly designed, perform within tolerance, require minimal maintenance, and be readily serviceable. Additionally, the manufacturer must be able to assist the customer in emergency situations. These areas have been given consideration and are also discussed.

[1]By definition, a parametric system includes the detecting function (sensor) and the signal conditioning function (in this instance, the MV/V). The detecting function includes temperature compensators.

SECTION II

CONCLUSIONS

OVERALL

The system can be productively employed in a treatment process provided the manufacturer's instruction are followed.

SENSOR

1. Two sensors were investigated and both failed after 3 months of operation. Neither operated over its expected "life without maintenance of 6 months." After 3 months, sludge accumulated at the cathode and dismantling of the sensor was required to clean the sludge and obtain satisfactory operation.

2. The "O" ring must be seated exactly in the sensor-head groove to prevent water seepage into the electronics.

3. The recessed stem-nut requires lubrication to be removed to permit sensor maintenance.

4. Temperature compensation potentiometers located in the sensor head prevent an exacting temperature compensation calibration.

5. Long-term transient response (2-24 hours) is dependent upon initial and final conditions.

6. Thermistors in the sensor head must be verified for proper positioning, and cable connection between the MV/V and different sensors must be identified in accordance to the Honeywell catalog.

7. Manual cleaning of the sensor caused 60 percent full scale spikes to occur which lasted several hours. Spikes did not occur when sensor maintenance was performed in a low pH (2.5) solution with minimal mechanical wiping.

8. Mechanical mounting of the sensor in the aeration basin determines the amount of air bubbles trapped on the sensor membrane. Near horizontal mounting of the sensor is preferred.

9. The sensors performed within the specifications for transient response, and were within tolerance for the temperation compensation tests.

10. With daily maintenance, sensor performance in activated sludge was acceptable--the unbiased standard deviation between the Winkler determination and the Honeywell reading was 0.256.

11. The sensors can be operated without maintenance for over a week in a chlorinated effluent.

MV/V[a]

1. The MV/V displayed an apparent shift of 40.3 to 40.9 percent at 35F (1.7C), and 41.2 to 42.9 percent at 65F (18.3C) or 1.5 percent between the worst conditions at each temperature before the chamber overheated.

2. The apparent shift after the chamber temperature excursion was 43.2 to 43.5 percent at 35F (1.7C), 42.6 to 43.1 percent at 65F (18.3C), and 43.5 to 44.0 percent at 95F (34C). The apparent shift between the worst cases for the total temperature range was 0.9 percent, which verified Honeywell's opinion that the 200F (93.4C) temperature in the chamber had not damaged the MV/V.

3. The independent linearity of the panel meter for the low and high ranges was a nominal 1.0 percent and 2.0 percent, respectively.

4. The panel meter display could not be easily seen from several feet away which meant it could not be mounted on a wall where physical contact could not be made. Panel meter indications are on the plastic cover plate, a position that increases the probability of error due to parallax.

5. Because of mechanical arrangement and location, the potentiometers on the range card could not be easily adjusted.

6. Parametric system performance in the final settling basin at the treatment plant was not satisfactory because there was no flow past the sensor. However, manual movement of the sensor produced performance comparable to other instrumental measurements of DO.

7. The sensor reduction potential was stable within 0.25 percent over a 2-week period and the MV/V response was in tolerance for step changes, and for filtering noise. The multivibrator 200 Hz frequency chosen was optimum in comparison to 100 Hz and 400 Hz.

[a]Millivolt to voltage converter function.

Although overall linearity was within specification (±2 percent), it varied by 0.5 percent between laboratory and field work. Performance employing different cable lengths met the manufacturer's specifications. And lastly, attenuation of power frequency noise fully met the manufacturer's specifications.

MANUALS AND SERVICE

The Honeywell manuals met or exceeded Section 5.00 of EPA's specifications for an integrated system and contained a summary of technical information to enable a broad spectrum of users to effectively employ the product. The local and main offices* of Honeywell were available for either hardware or technical explanation as the need occurred.

*Honeywell, Fort Washington, Philadelphia, Pennsylvania.

SECTION III

RECOMMENDATIONS

The recommendations summarised are directed to three product areas:

A. The manufacturer should:

1. Provide the customer with two options: automatic sensor cleaning and a small submersible pump to maintain sample velocity (parallel) over the membrane. Both devices would be attachable to the submerged sensor.

2. If the sensor must be cleaned manually, define the exact method to reduce "spikes" following maintenance.

3. Relocate the temperature compensating potentiometer in the MV/V. If this cannot be done, simplified temperature calibration procedures for submerged sensor operation must be developed.

4. Clarify the notations on the circuit diagrams so that there is only one subscripted variable, such as TP-1, per system.

5. Reconsider the overall design since the same measurement can be effected with fewer electronic components.

6. Simplify the page numbering system in the manual.

7. Spare "O" rings and sealant material for the sensor head should be provided.

8. Define methods of installation unique to the application and employ drawings or their equivalent.

9. Locate meter markings on the panel face rather than on the cover plate or provide a mirror at the back to eliminate parallax. A digital readout would be helpful.

10. Determine the linearity of the MV/V at 35, 65, and 95F (1.8, 18.3, 35C) and publish the data in the manual.

11. Provide a screwdriver in the kit to adjust the MV/V potentiometers.

12. Reevaluate the manuals and correct small errors without losing the tutorial characteristics.

B. The prospective user should:

1. Define basic requirements for DO measurement so that Honeywell can provide appropriate system functions.

2. Study the manuals thoroughly before attempting to use system.

3. Random errors occur in both Winkler and instrument determinations; so that an exact correlation between the two methods is not to be expected.

4. Establish a strong communication link with the manufacturer. This will save money over a period of time.

5. Expect to achieve results similar to those summarized in this document.

6. Expect periodic manual maintenance although automatic cleaning is also provided.

C. The final user should:

1. Develop a well-disciplined maintenance program based on the manufacturer's recommendations. If the system is comparable to the one investigated and the sensor is installed in activated sludge, daily maintenance is required. Weekly maintenance is recommended if it is placed in a chlorinated effluent. More frequent maintenance may be required if the sensor is installed in an effluent raceway (if untreated samples are diverted there).

2. Keep logs on application, performance, method of installation (contact the manufacturer), flow, liquor constituents, air volume, and other appropriate parameters. Inform the manufacturer of measurement and sample characteristics; this information can be considered when new models are being designed.

3. Follow the manufacturer's written recommendations exactly. If the system fails to provide the performance expected, contact the manufacturer.

4. If auxiliary flow is provided, discuss with the manufacturer the proper flow vector in relation to the membrane because the angle of flow directed at the membrane depends on the physical design (Honeywell recommends a 45° angle).

5. Determine the presence of air bubbles on sensor. These cause spikes in output and can cause incorrect control (see No. 2 under Recommendations for Manufacturer).

6. Analyse probable fault before making potentiometric adjustments.

7. Consider having the manufacturer carry out maintenance operations under contract if manpower is in short supply.

8. Install the MV/V in a pump house to protect it from the weather and calibrate the unit monthly.

SECTION IV

OVERVIEW OF THE HONEYWELL DO PARAMETRIC SYSTEM

The Honeywell parametric system consists of an in situ sensor assembly, 50 feet (15 m) of four-conductor-shielded cabling, and a MV/V transmitter.

SENSOR ASSEMBLY

Honeywell's sensor design philosophy permits a general-purpose MV/V to be used because the sensor assembly produces a mv potential signal that is proportional to the DO concentration. The sensor assembly has two main functional components, the DO detector and the temperature-compensating network.[1,2] The components are listed in Table 1.

Table 1. COMPONENTS OF DO SENSOR

Cathode	1/8" diameter: silver-platinum-gold
Anode	Silver
A/C ratio	400, nominal
Body	PVC
Thermistor	Exposed to sample (R_0 @ 65F = 500 Ω)
Membrane	1 mi teflon
Electrolyte	0.5 N KOH + 2.0 N KCl
Reduction potential	800 mv, fixed
Temperature-compensating potentiometer	Adjustable
Other	Discussed in patent.

A wiring diagram of the sensor assembly is shown in Figure 1, and a simplified schematic is shown in Figure 2.

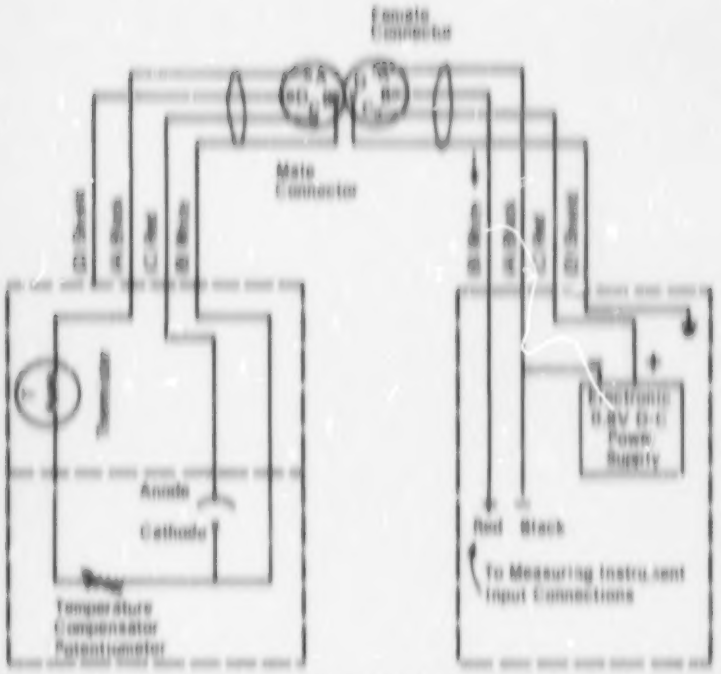


FIGURE 1. SUBMERSIBLE TYPE DO SENSOR, WIRING DIAGRAM WITH EXTERNAL CIRCUITS IN MEASURING INSTRUMENT.

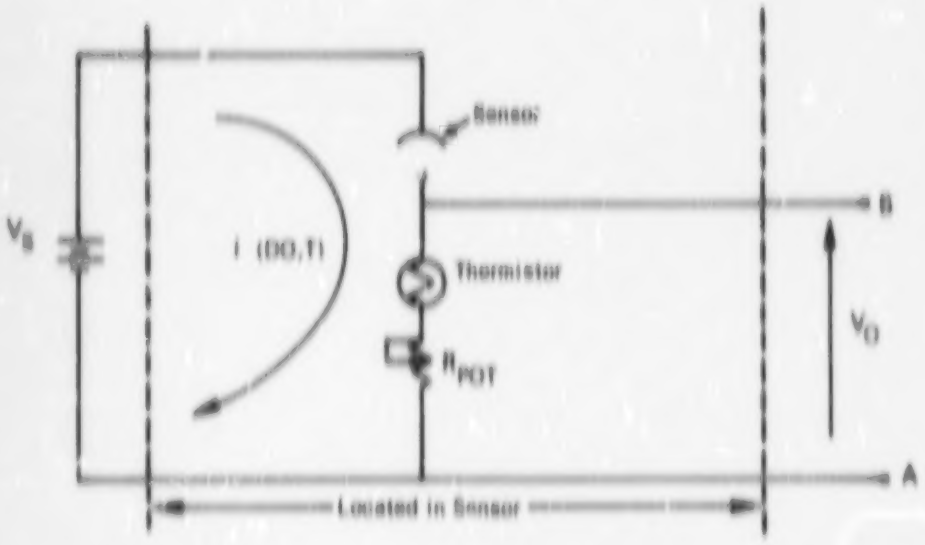


FIGURE 2. SIMPLIFIED SCHEMATIC OF THE HONEYWELL SENSOR'S CIRCUITRY.

If it is assumed that the impedance connected to terminals B and A is much greater than $R_{pot} + R_{th}$ for all temperatures, the steady-state output potential is:

$$V_o = i\,(Bu,T) \times (R_{pot} + R_{th}\,(T)) \qquad (1)$$

where V_o = sensor assembly signal, volts

$i(Bu,T)$ = current proportional to Bu concentration and temperature, amperes

R_{pot} = trim potentiometer, ohms

$R_{th}(T)$ = temperature-sensitive thermistor, ohms

T = degrees Kelvin

For fresh water and considering the temperature dependency noted by equations B-7 and B-8 in Appendix B equation 2 is obtained.

$$V_o = iKe^{-\frac{J}{T}} \times \left(R_{pot} + R_o e^{+\frac{B}{T}}\right) \qquad (2)$$

where K, J, and B = constants of proportionality

R_o = reference resistance, ohms

Equation 2 can be rewritten:

$$V_o = iKR_{pot}e^{-\frac{J}{T}} + iKR_o e^{\frac{B-J}{T}} \qquad (3)$$

it appears, therefore, that the Honeywell sensor[6] is not completely temperature compensated, since, assuming B and J are equal:

$$V_o = iKR_{pot}e^{-\frac{J}{T}} + iKR_o \qquad (4)$$

However, equation 2 is theoretically ideal and Honeywell (as well as most other manufacturers) follows R. Bates'[3] philosophy of an operational definition employed in pH determinations: the total parametric system, including temperature compensation, is calibrated in accordance with the Winkler process[7] and at saturated conditions. Thus, if the sensor is immersed in a comparable sample it produces an output considered to be proportional to the DO concentration, within acceptable tolerances.

EPA's long-term practice has been to temperature compensate and calibrate the parametric system under fresh water "saturated" conditions at 35, 65, and 95F (1.7, 18.4, 35C). (The results will be discussed later.) In the field, trim on the gain control would be made following comparison of the Winkler and instrument determinations.

By schematically interchanging the temperature compensator and potentiometer, it would be possible to relocate the potentiometer within the analyser thereby minimising manhours involved in temperature compensation. Since the analyser is for general purposes, it may be necessary to intercept the black wire from Terminal A in Figure 1 and insert two separate plug-in posts, providing means for potentiometer insertion or a short circuit. (Honeywell uses a similar DO sensor design in its tank-type systems.)

MV/V TRANSMITTER

The MV/V converts a source mv potential into an output potential in the 0-5 VDC range. Table 3 lists some of the components displayed in Figure 3.

---

[6]When $R_o = R_{pot}$, the first term in equation 4 becomes negligible (within sensor tolerance) so that the output potential is effectively independent of temperature. And, additionally, for temperatures of interest, $J \gg T$.

†The process involves wet chemical techniques that culminate in the titration of free iodine. See Appendix A for further discussion.

Table 2. MV/V FUNCTIONAL COMPONENTS

1. Power distribution	5. Auxiliary power supply
2. Sensor power supply (800 mv)	6. Measuring circuit
3. Power supply analyser	7. Amplifier assembly
4. Control/alarm module	8. Isolation module
	9. Output function

1. (Refer to Manual).

2. Sensor power supply - This two-stage, zener-regulated DC supply provides a fixed 800 mv potential to the sensor. Conveniently located test points (TP_1 and TP_2 are used to verify the reduction potential. As noted by Gealt and Metarko, a slight change in the reduction potential has little or no effect on sensor output, therefore no trim pots are included.[4]

3. (Refer to Manual).

4. Control/alarm - This component was damaged in shipment, but since the authors had not planned to investigate it, the component was left unchanged. The alarm circuitry provides (1) an on - off controller function; (2) a separate HI - Low alarm, and (3) a combination of (1) and (2). EPA specifications provide for (2) within its Sample Taker parametric system but not for (1).[5] These features could be employed to control aeration in sewage treatment plants.

5. (Refer to Manual).

6. Measuring circuit - This function consists of potentiometers and divider networks having offset and gain capability. Additionally, the measuring circuit, which is connected to the negative terminal of the signal source, can be provided with input suppression and thermocouple compensation when required. The measuring circuit is provided with a 5-volt supply, whose temperature-stability data are discussed later. It is apparent that the MV/V has greater flexibility than a standard DO-type microammeter available in other designs. Thus, the available components should be matched with the engineering application to obtain maximum benefits.

7. Amplifier assembly - This is the main component in the MV/V, and it consists of a filter section, a solid state modulator-demodulator driven by a free running multivibrator, an AC amplifier,

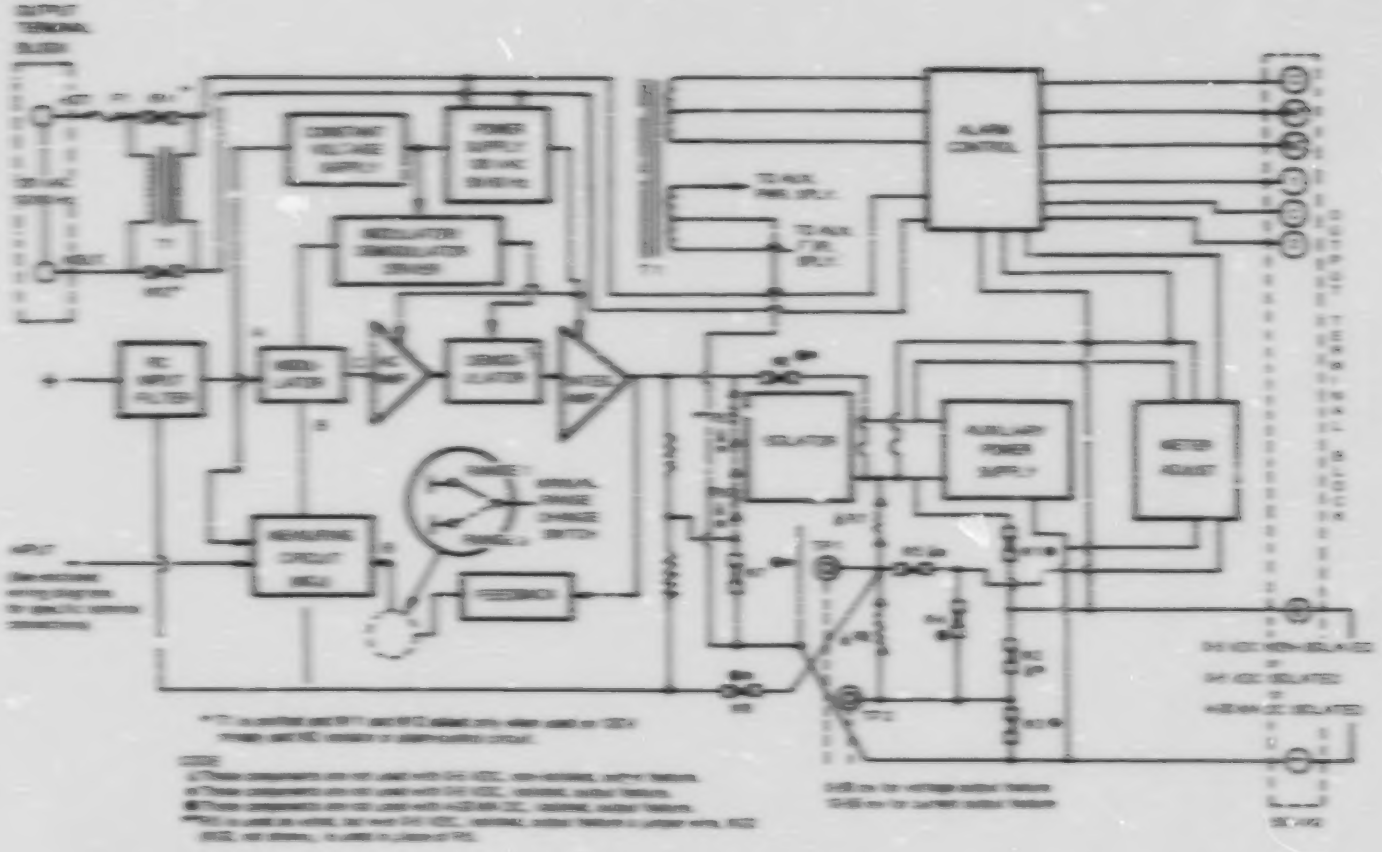


FIGURE 3. FUNCTIONAL LAYOUT OF MV V.

ard an integrating operational amplifier. The output drops the AC amplifier input to zero through the measuring circuits so that any error developed by a change in DC input causes a change in the potential of the integrating capacitor, hence change in output.

Sixty Hz noise has been a periodic problem in this type of instrumentation, but the following analysis shows that most of it is attenuated by the filter section.

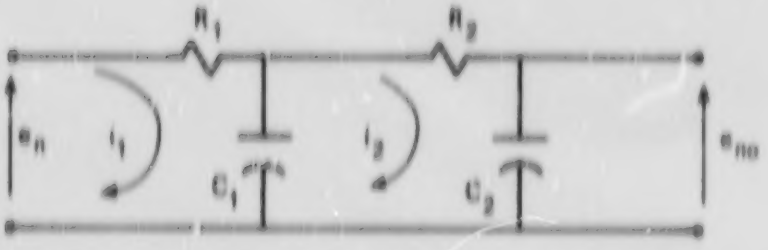


FIGURE 4. SIMPLIFIED DIAGRAM OF MV/V FILTER NETWORK.

Equation 5 and 6 are derived from Figure 4 as follows:

$$e_n = i_1 \left(R_1 + \frac{1}{j\omega C_1}\right) - i_2 \frac{1}{j\omega C_2} \tag{5}$$

$$0 = -i_1 \frac{1}{j\omega C_1} + i_2 \left(R_2 + \frac{1}{j\omega C_1} + \frac{1}{j\omega C_2}\right) \tag{6}$$

where $R_1 = R_2 = 10K$, ohms

$C_1 = C_2 = 4.7$ μfarads

i_1 and i_2 = instantaneous loop currents, amperes

It is assumed that e_n is a 60-Hz sinusoidal noise and that the load impedance approaches an open circuit.

Employing RMS notation, steady-state conditions are:

$$E_n = I_1 \left(R_1 + \frac{1}{j\omega C_1}\right) - I_2 \left(\frac{1}{j\omega C_2}\right) \tag{7}$$

$$0 = -I_1 \left(\frac{1}{j\omega C_1}\right) + I_2 \left(R_2 + \frac{1}{j\omega C_1} + \frac{1}{j\omega C_2}\right) \tag{8}$$

Equations 7 and 8 yield the current through C_2, and the approximate steady-state output voltage, E_{o_n}, is then given by:

$$E_{o_n} = I_2 \frac{1}{j\omega C_2} = \frac{E_1}{1 - (R\omega C)^2 + j3R\omega C} \tag{9}$$

An assumed noise of 3 mv yields a filter output of approximately 9.6 microvolts. Thus, if noise appears in a recording function, it is probably caused by output shielding rather than the input filter--presuming that all filter components are performing within tolerance. A plot of equation 9 is shown in Figure 5.

The amplifier, which is equipped with a panel meter display, can provide either current or voltage outputs, depending on bid specifications and application. The MW/S investigated provided 0-50 mv and 0-5 VDC outputs.

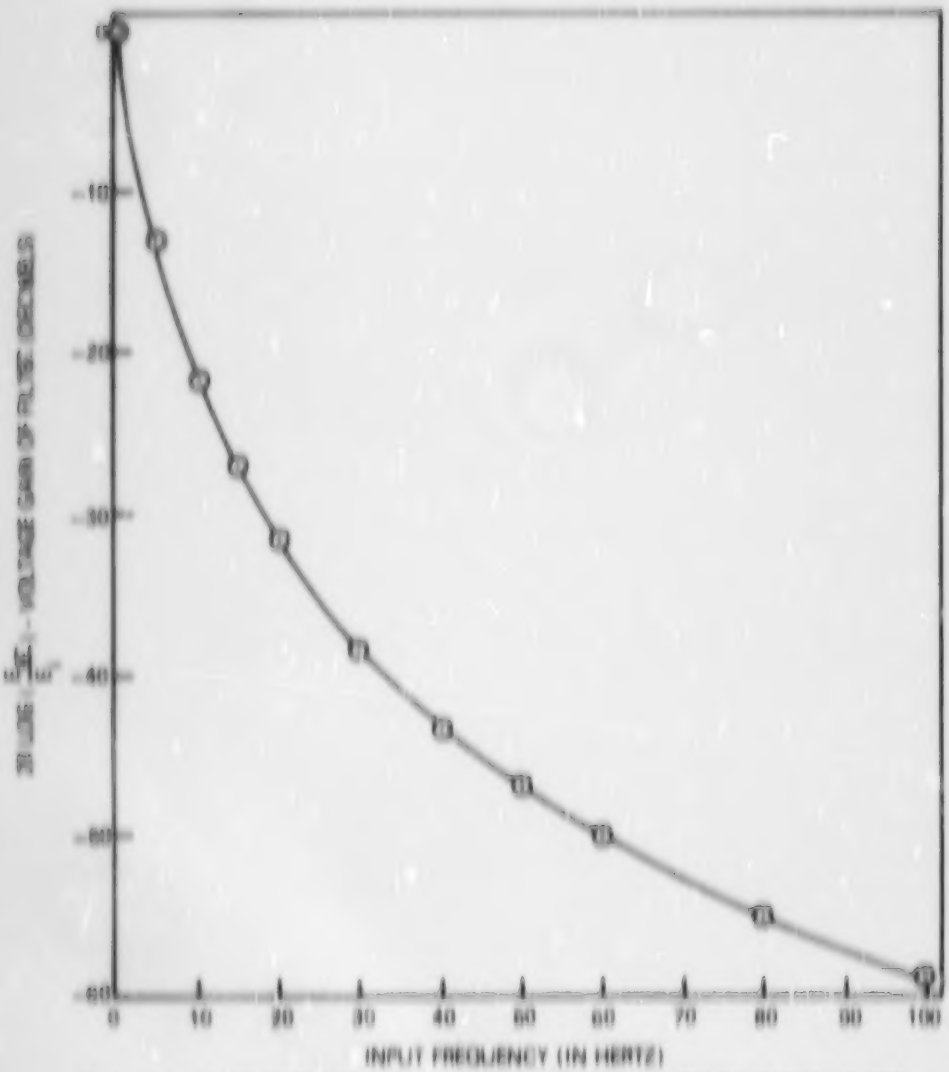


FIGURE 9. THEORETICAL FREQUENCY RESPONSE OF MV/V INPUT FILTER.

Simply stated, the amplifier assembly can be thought of as a gain/offset device described by equation 10:

$$DO = KG(j\omega)V_i + MV_o \qquad (10)$$

where DO = dissolved oxygen in mg/l (output)

K,G,m = constants of proportionality

V_i = input potential, mv

V_o = offset potential, mv

$j\omega$ = complex notation, variable frequency

For the DC steady-state condition, equation 10 reduces to:

$$DO = K_2V_i + mVO \qquad (11)$$

where K_2 = constant of proportionality.

Hence, the amplifier is a two-control device having span (K_2) and offset (m) potentiometers (Figure 6).

8. (Refer to Manual).

9. (Refer to Manual).

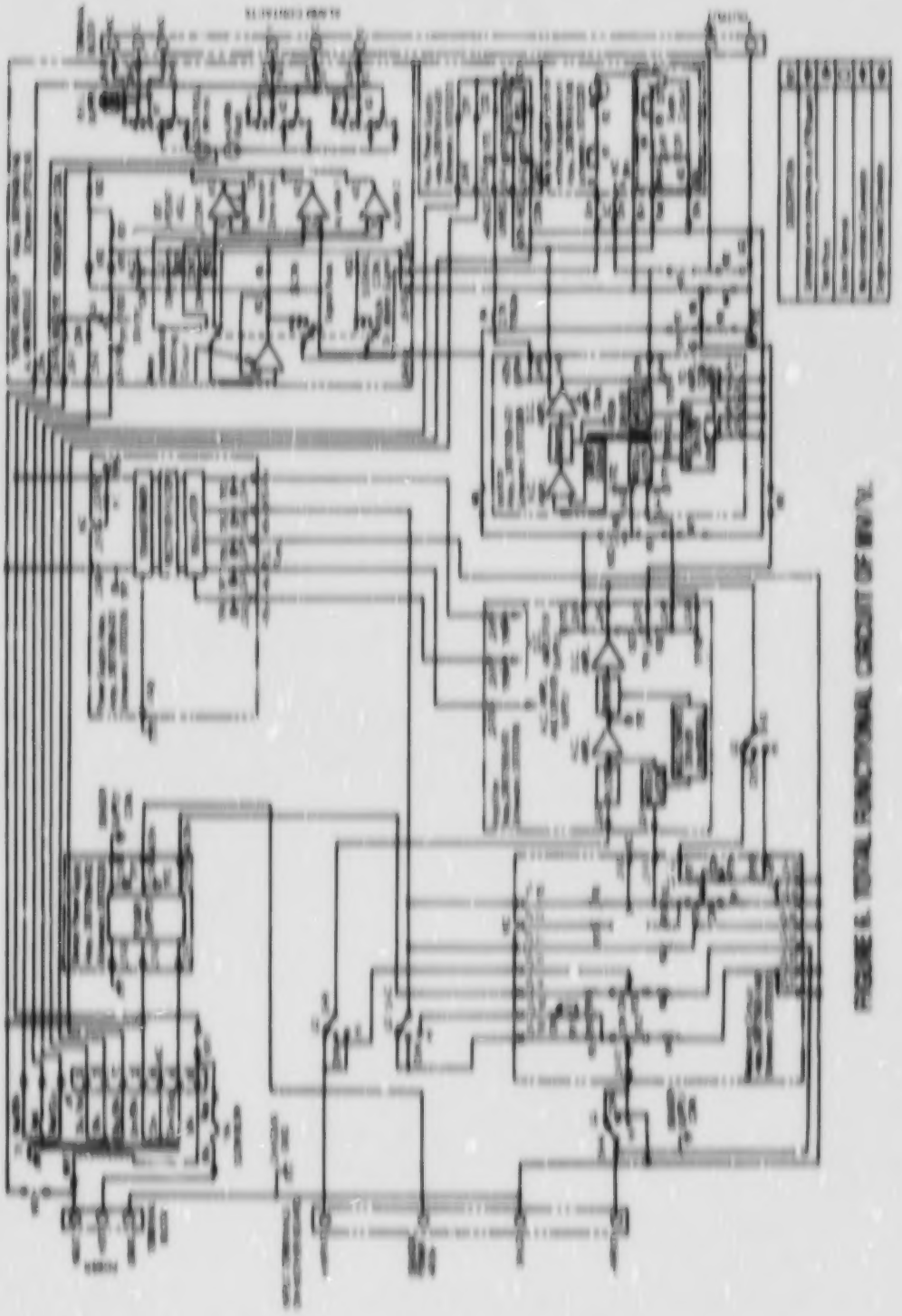


FIGURE 4. TYPICAL FUNCTIONAL CIRCUIT DIAGRAM

SECTION V

LABORATORY INVESTIGATION

To accommodate EMSL's test procedures, Honeywell field changed the MV/V range card from 0-5 and 0-10 mg/l DO to 0-12 and 0-24 mg/l on the low and high ranges, respectively, a modification that required a two-point recalibration. The panel meter markings were left unchanged, therefore 10 corresponds to 100 percent full scale for both ranges. The data for this recalibration are shown in Table 3. Data between these limits for linearity are shown further on.

Table 3. ROOM TEMPERATURE ZERO AND SPAN CALIBRATION FOR THE MV/V[a]

Input (10^{-3} volts)	Range	PM	Output (10^{-3} volts)[b]
0	low	0	10
0	high	0	10
6.6	low	10	50
13.2	high	10	50

[a]Honeywell recommends that the sensor assembly and the MV/V be calibrated as an integrated unit. For this test and several others, it was convenient to work with each separately.

[b]Measured between TP-1 and TP-2.

SENSOR ASSEMBLY INVESTIGATION

Two sensor assemblies were investigated for their temperature-compensation and short- and long-transient responses. The MV/V was employed in temperature-compensation tests. Two assemblies were investigated due to failure noted below. Three Forma baths similar to the one shown in Figure 7 were used. Each contained 7.5 liters of distilled water that was adjusted to 41F, 65F, and 95F (5C, 18.3C, 35C) and held constant within 1.0F (0.5C). Each bath was aerated with atmospheric gases, and diffusors provided a reasonably consistent distribution.

Several test procedures were employed before satisfactory data were obtained. The first employed the polyethylene bottle shown in Figure 8 that was modified several times, such as adding holes to the top

permitting escape of trapped gases. The second modification employed a horizontal aluminum frame but slight dimensional differences in the Forma baths allowed movement of the frame and change in relative position of the sensor tip with respect to the sample stream. Transient and long-term stability data for sensor 2 were obtained with the last and most favorable modification shown in Figure 9. Each Forma bath was marked for the precise location of the supporting pipe so that regardless of the bath employed, the sensor tip was always in the main stream line of the sample flow with the stream line 10" below membrane surface.

The sample velocity from each flow nozzle, as measured by a March-McBirney velocity meter Model 201, was 1.5 feet per second at cold, room, and high temperatures.

Sensor 1

One problem encountered in designing DO parametric systems is providing an inexpensive and conveniently located temperature-compensation circuit to correct for the membrane permeability factor illustrated by equations 1-4.

The temperature-compensation technique was investigated by adjusting the zero and span controls in the MV/V and the potentiometer R_{pot} in the sensor assembly. Data taken following initial experimentation and after final potentiometric adjustments are shown in Table 4.

Table 4. CALIBRATION DATA OF THE HONEYWELL DO PARAMETRIC SYSTEM EMPLOYING SENSOR 1

Temperature C	Winkler DO determination mg/l	Output-high range indicated DO mg/l	
		before	after
6	12.50	12.6	12.50
19	9.40	9.5	9.30
38	6.80	6.7	6.60

Temperature compensation was difficult to achieve, because after each adjustment the sensor head had to be replaced and validity of the test setup had to be reconfirmed. This occurred several times for each measurement.

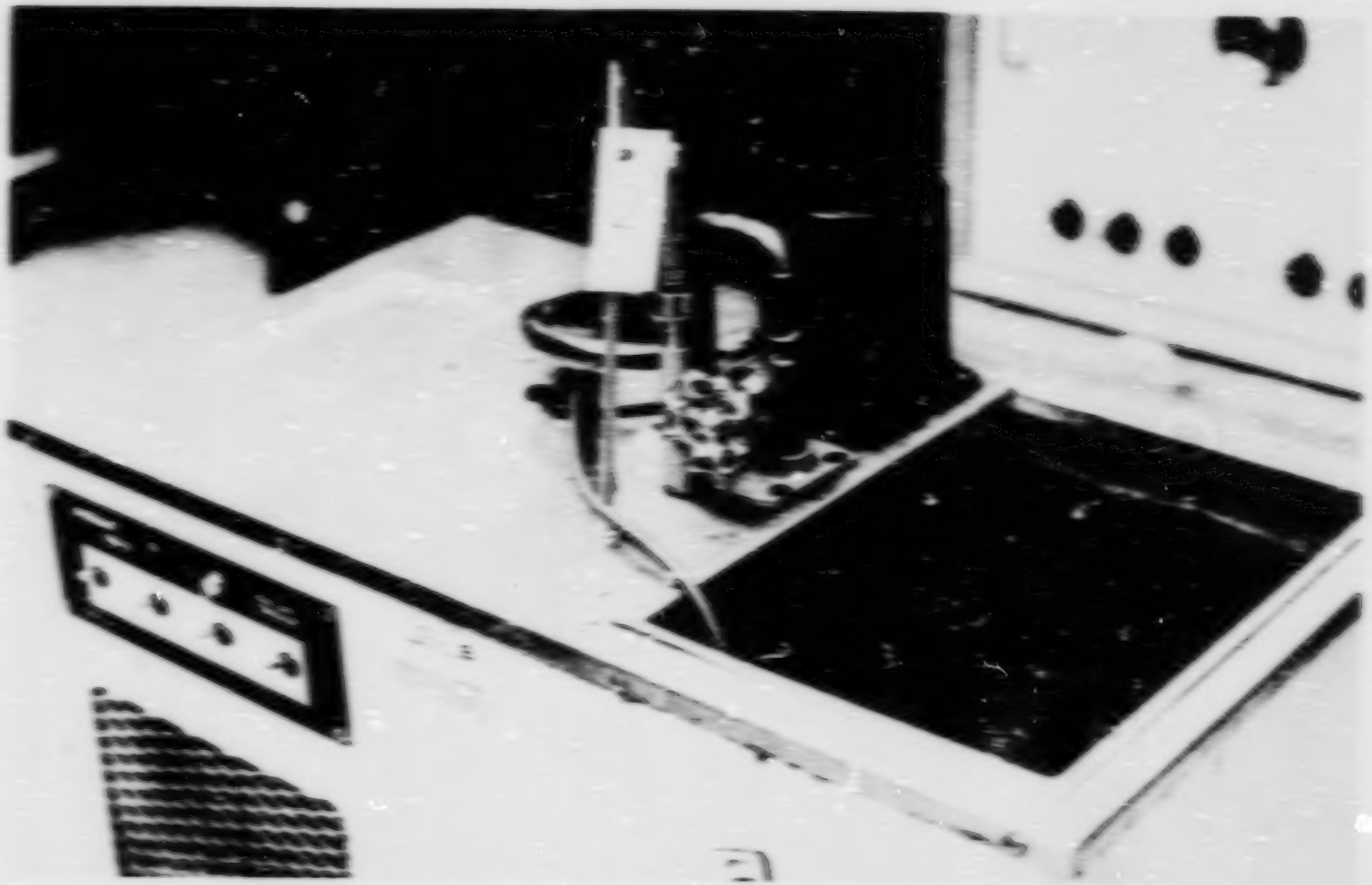


FIGURE 7. POWER BATH FOR TEMPERATURE-COMPENSATION AND THERMAL RESPONSE.

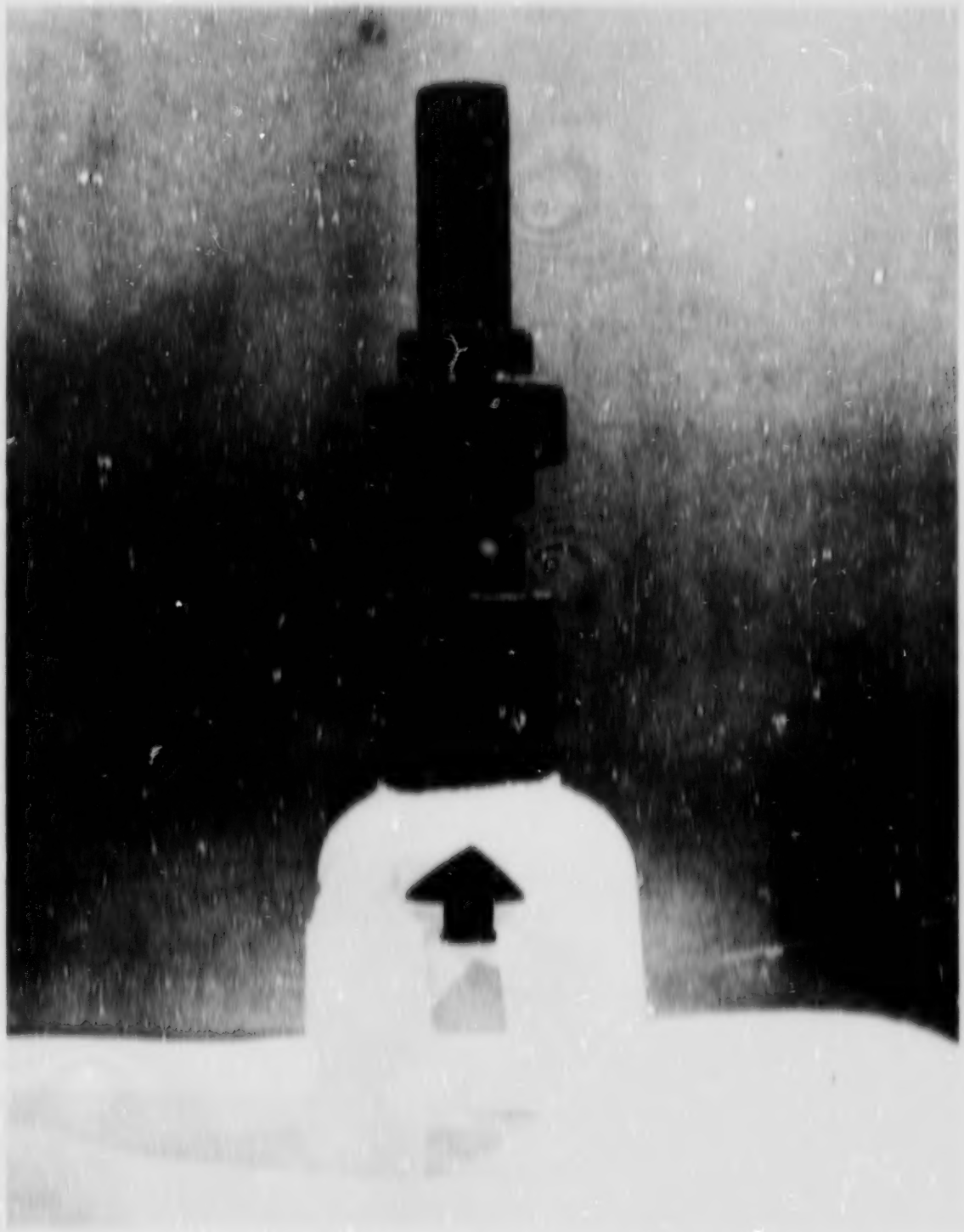


FIGURE 8. FIRST SENSOR ASSEMBLY CONFIGURATION (THE POLYETHYLENE BOTTLE WAS LATER MODIFIED).

FIGURE 9. PIPE SUPPORT SYSTEM FOR SENSOR ASSEMBLY.

The deviation between instrument data and the Winkler DO determination was less than 1.0 percent of full scale for both the "before" and "after" tests. (Honeywell calibrated the sensor when it was partially submerged, but the data in Table 4 were obtained while the sensor was fully submerged.)

Transient Response Procedure

Transient response data magnify any quirk in (1) design, (2) manufacture, or (3) the investigation process. Transient data accumulated on the Honeywell sensor assembly reflected the influence of all three: (1) the trim pot should be relocated into the MV/V; (2) sensor 1 failed, and the thermistor was not properly installed in sensor 2--it rotated during the preliminary tests; (3) tests were repeated several times because of unsatisfactory conditions, such as the flow moving the sensor and the improper alignment of the assembly over the flow. The latter yielded a sinusoidal superimposed on an exponential that invalidated the response. The latter was eventually corrected by the piping arrangement shown in Figure 9.

Transient responses to temperature and DO concentration were obtained by rapidly transferring the sensor assembly from one bath to another. The procedures listed in Table 5 were followed in investigating both sensor assemblies.

Table 5. TRANSIENT RESPONSE PROCEDURES

Sensor in bath	Winkler taken from
--	RT (initial)
RT	CT before transfer
CT	RT after "
CT	HT before "
RT	CT after "
RT	HT before "
HT	RT after "
HT	RT before "
RT	HT after "
--	RT (final)

CT = cold temperature = 5C (varied between 1.7C and 5C, and noted, due to ice formation on the refrigerant coils).
RT = room temperature = 18C.
HT = hot temperature = 35C.
Sensor transfer = RT-CT-RT-HT-RT

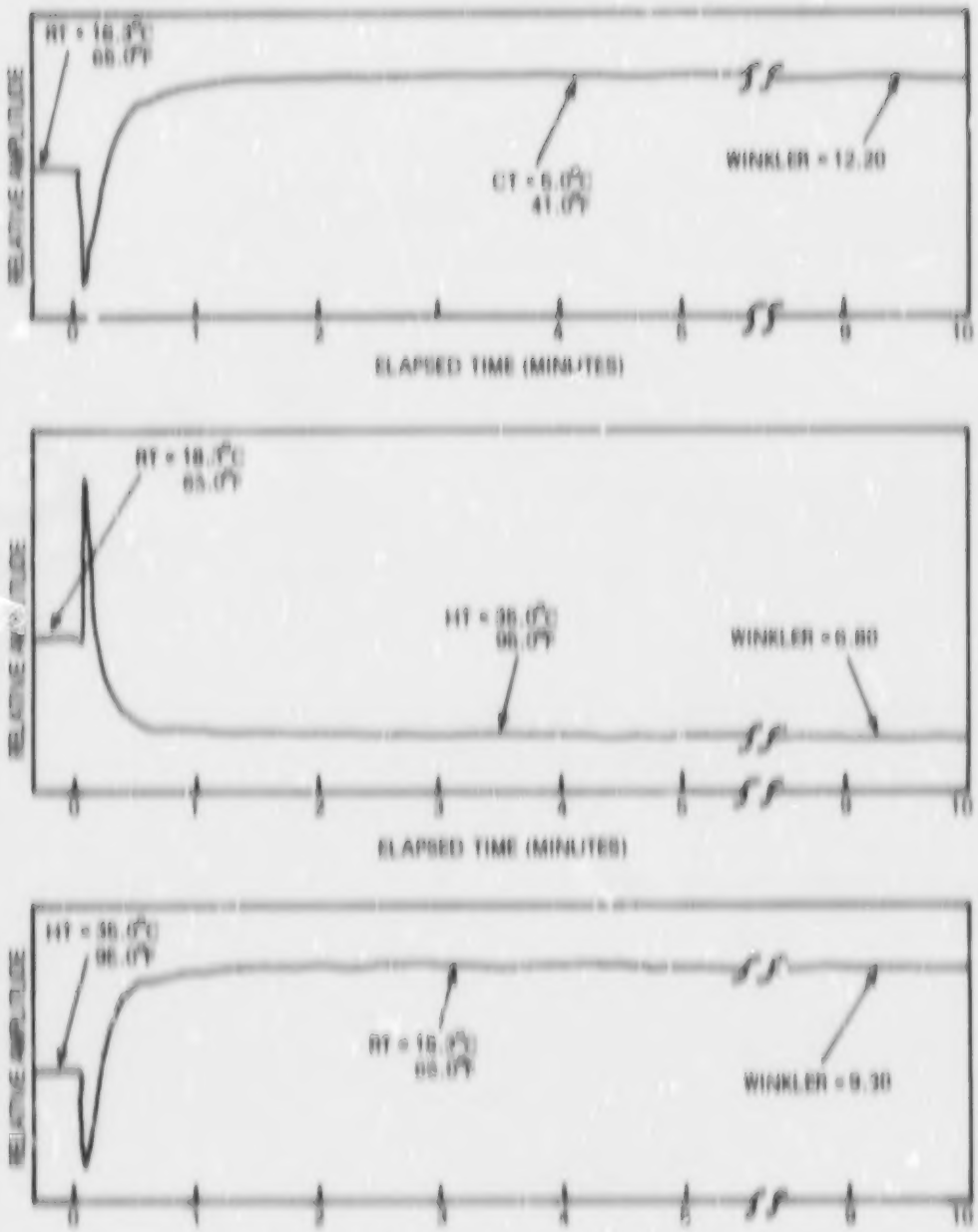


FIGURE 10. SHORT-TERM RESPONSE OF SENSOR 1.

Results of Transient Response Investigation - The short-response (10-min) capability of sensor 1 is displayed in Figure 10. Slight irregularities were caused by imperfect test facilities; but the output appeared to be within Honeywell's tolerance at 3 minutes as related to the 10-minute value. Data were collected on an Esterline Angus Speed Servo recorder operated at 0.75 inch per minute chart speed.

The response curves are comparable to those recorded during previous investigations except for the top graph in Figure 10; the overshoot was much less than that observed for other sensor designs (see discussion on Sensor 3).

Failure - Long-term (>60 min) responses were attempted but were unsatisfactory because of: (1) changes in the sensor's orientation; (2) recorder inking problems; and (3) a "noisy" sensor.

Problems (1) and (2) were resolved in-house, but (3) could not be corrected, and a replacement sensor was provided.

Figure 11A illustrates the cathode before the sensor was placed in operation. Figures 11B and 11C show its condition after several tests over a 2-week period.

Following discussions with Honeywell,[6] the pH of the electrolyte was determined to be 10, but the discoloration of the cathode was of a sludge nature and not a "plating-out" phenomenon. To accumulate more residue at the cathode, the sensor was energized by 80 mv and immersed in a saturated, distilled-water sample at 95C (35C). After 2 weeks, the cathode appeared as shown in Figure 11D; once again, the discoloration was of a sludge nature, but slightly more had accumulated. It appeared that either the screen described in Gealt's patent did not function as expected or that it had been improperly installed (no work was performed to determine the cause of the accumulation, presumably AgCl).

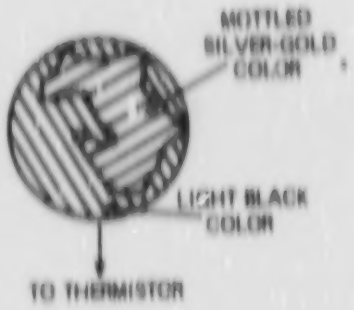
(In subsequent discussions, Gealt said that several sensors, including the one tested, were manufactured employing a different assembly technique--only one end was supported during assembly, and this had caused the screen and cathode element to be slightly out of line. As a result, more frequent (within 12-15 weeks) service was required. He indicated that a revised assembly process was being employed.)

Photographs of sensors 1 and 2 appear in Figure 12.

A. SENSOR CATHODE AS RECEIVED

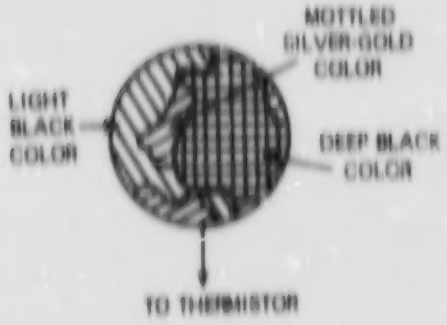
HAS UNDERGONE ONLY FACTORY CALIBRATION

B. SENSOR CATHODE AFTER TRANSIENTS



HAS UNDERGONE LABORATORY CALIBRATION, TEMPERATURE COMPENSATION, AND TRANSIENT RESPONSES

C. SENSOR CATHODE 2 WEEKS AFTER EXPOSURE TO 95°F(35°C)



DISTILLED H_2O BATH, D.O SATURATED, AT 95°F(35°C)

D. SENSOR CATHODE 4 WEEKS AFTER PROLONGED EXPOSURE TO 95°F(35°C)

FINAL APPEARANCE AT 8/20/74

FIGURE 11. SLUDGE ACCUMULATION ON CATHODE OF SENSOR 1.

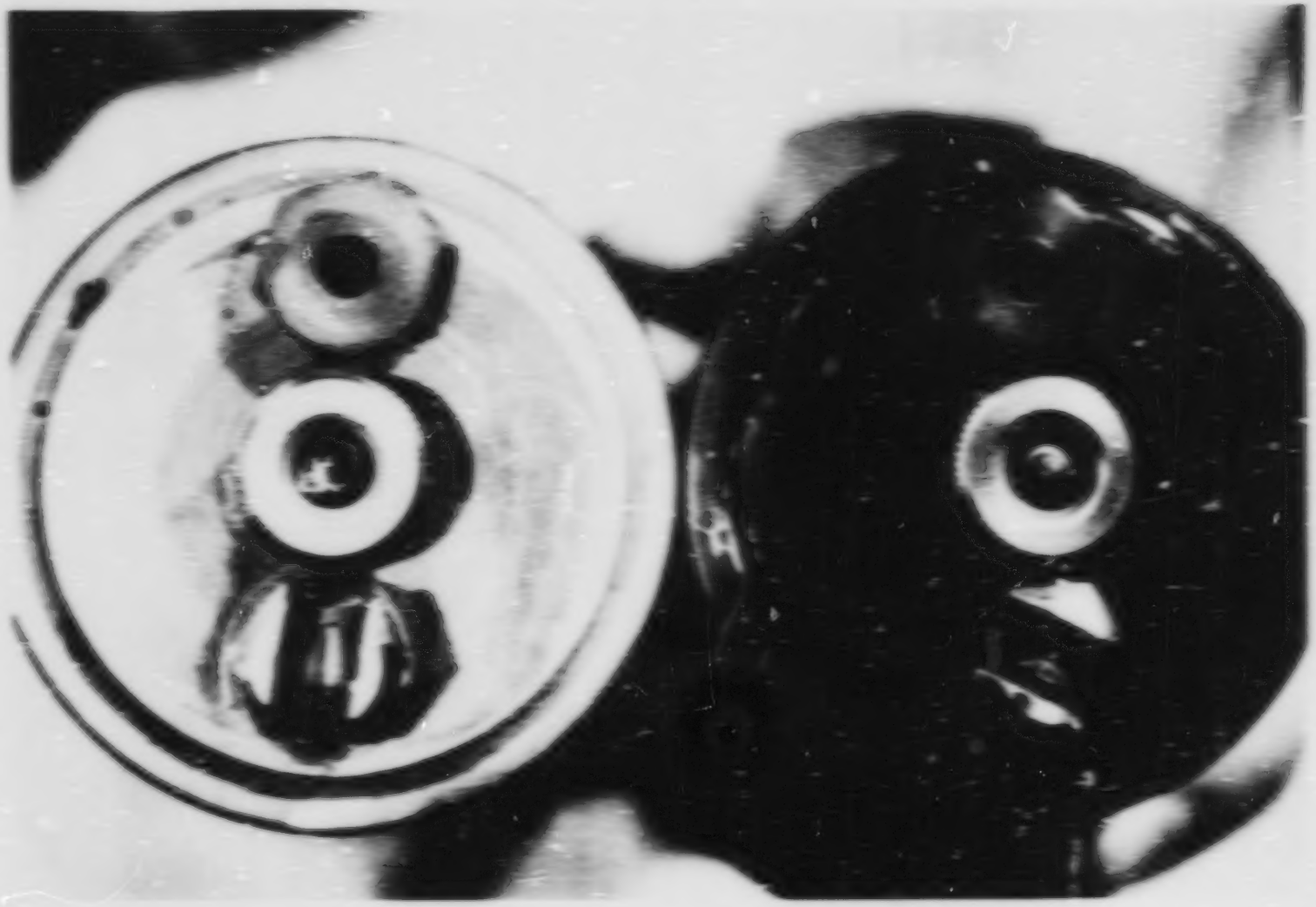


FIGURE 12. PHOTOGRAPHS OF SENSORS 1 AND 2.

Sensor 2

Sensor 2 was subjected to similar tests but their duration and sequence differed:

1. Laboratory (initial calibration of parametric system).
2. Field investigation (parametric system).
3. Service on sensor (sensor assembly).
4. Field investigation (parametric system).
5. Laboratory (sensor assembly only):
   (a) 10- and 60-minute response and 24-hour stability
   (b) service on sensor
   (c) with and without pressure diaphragm.

Items 2, 3, and 4 are discussed later.

Laboratory (Initial Calibration of Parametric System) - Saturated samples maintained at a constant temperature, as described earlier, were used. All available controls (R_{cal}, zero, and span) were employed, and the MV/V panel meter reading was recorded. The sensor assembly was maintained in each sample for a nominal 24 hours. The results are summarized in Table 6.

Table 6. CALIBRATION DATA FOR THE HONEYWELL DO PARAMETRIC SYSTEM EMPLOYING SENSOR 2 (STEADY STATE, AFTER 24 HOURS)

Temperature, C	Winkler DO, mg/l	PM-Hi range DO, mg/l
CT 4.9	12.75	12.60
RT 18.3	9.45	9.41
HT 35.0	6.95	6.80

Data in Table 6 are within EPA's tolerance of ±0.24 mg/l.

Output from the sensor assembly was recorded on an Esterline Angus recorder, and the steady-state values are illustrated in Figure 15.

Laboratory (Sensor Assembly Only) - Following the field work, the sensor assembly was stored in the laboratory for several weeks during which time the stability of the 800 mv reduction supply was investigated. This potential "lies on the center" of the polarographic

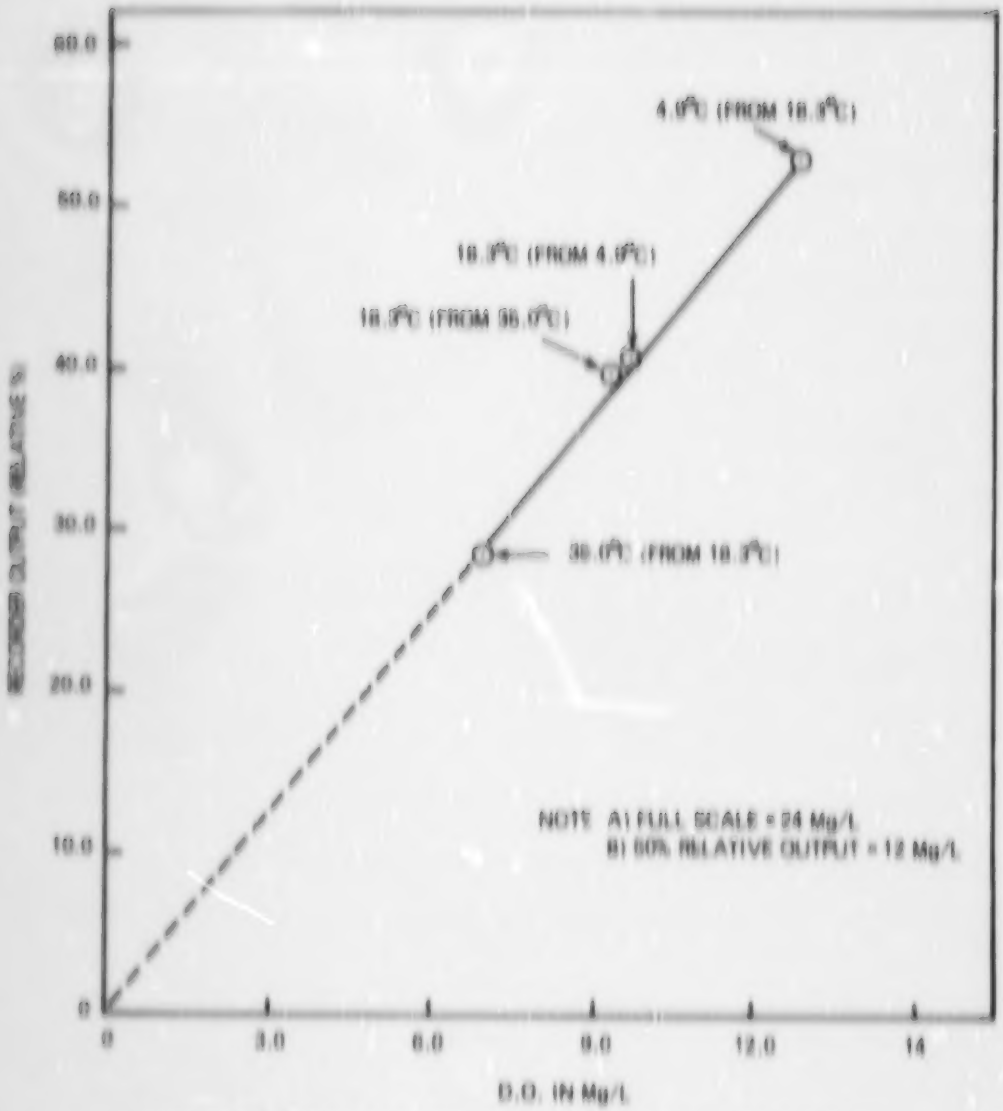


FIGURE 13. TEMPERATURE COMPENSATION OF SENSOR ASSEMBLY.

plateau, which reduces the effects caused by slight voltage fluctuations. Honeywell does not, therefore, provide potentiometric adjustments. Figure 14 illustrates the stability of the 800 mv supply.

The response and the 24-hour stability of the sensor assembly are illustrated in Figures 15-17 for the RT→CT, CT→RT, and RT→HT modes.

Inspection of Figures 15, 16, and 17 reveals that at 2 minutes the sensor output was within 98 percent of the output recorded at approximately 1 hour and that in all cases the sensor output was within Honeywell's tolerances at 24 hours.

An apparent maximum overshoot approached 5 percent at 10 minutes for the RT→CT transient, and those for the CT→RT and RT→HT modes approximated 1 percent. The CT DO level decreased 1 percent during the last 23 hours of the stability run, therefore the overall overshoot for the RT→CT test may have been less than 5 percent.

The temperature and the DO concentration at room temperature varied and caused a slight change in the output. The differences between the Winkler DO determination and the Honeywell measurement were less than 1 percent.

All three response curves indicate, therefore, that the thermal response was within Honeywell's tolerances and met the 24-hour stability criterion.

The initial decrease in Figure 15 is caused by the teflon as the diffusion of oxygen through it is more rapidly affected by temperature than the compensating resistance of the thermistor. Treating the sensor as a constant-current generator for given conditions, the output voltage across the thermistor-potentiometer circuit increased, as displayed by the graph.

Regardless of the final DO level, several tests indicated that the RT→CT response, although within 98 percent of steady-state at 2 minutes, did not reach 100 percent steady-state for several hours. This was thought to be related to the total sensor heat capacity (PVC, electrolyte) as well as to possible thermal affects of the teflon. No work was performed to isolate and study these possibilities.

The response curves in Figures 16 and 17 are similar since in both cases the sensor assembly was transferred to a warmer sample. The initial positive pulse apparently occurred because the thermal response of the membrane resulted in greater diffusion of DO to the

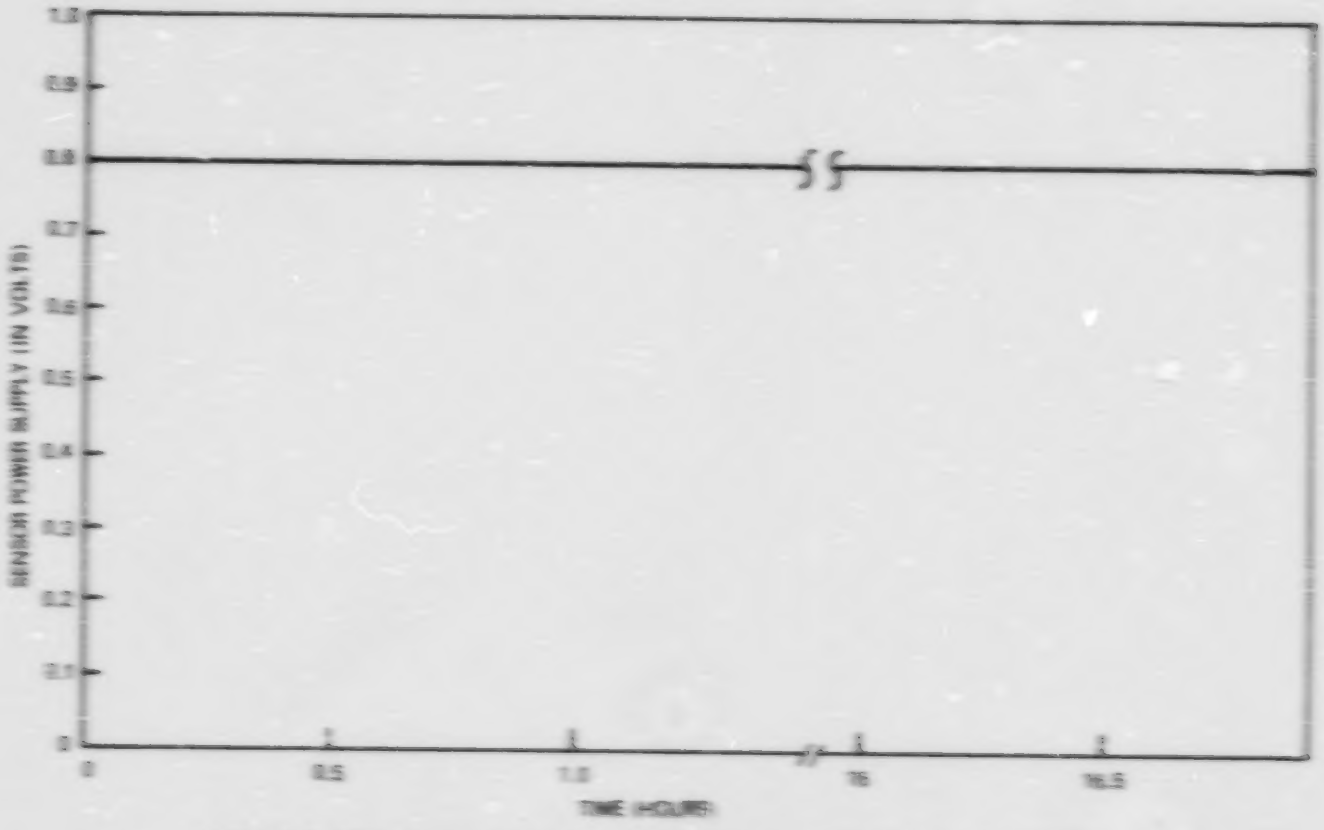


FIGURE 14. ROOM-TEMPERATURE STABILITY OF EROSION REDUCTION POTENTIAL

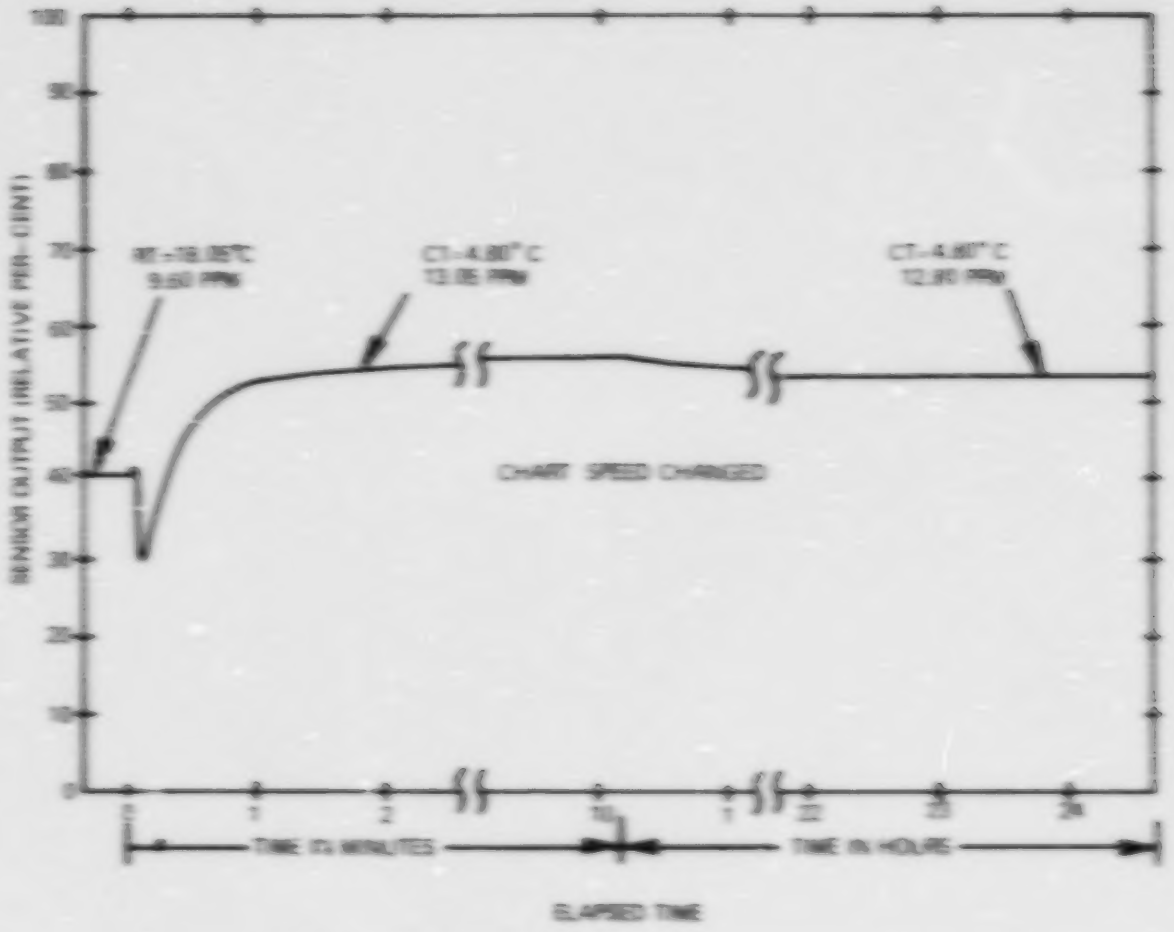


FIGURE 15. TWENTY-FOUR TOTAL SESSION RESPONSE (RT-CT).

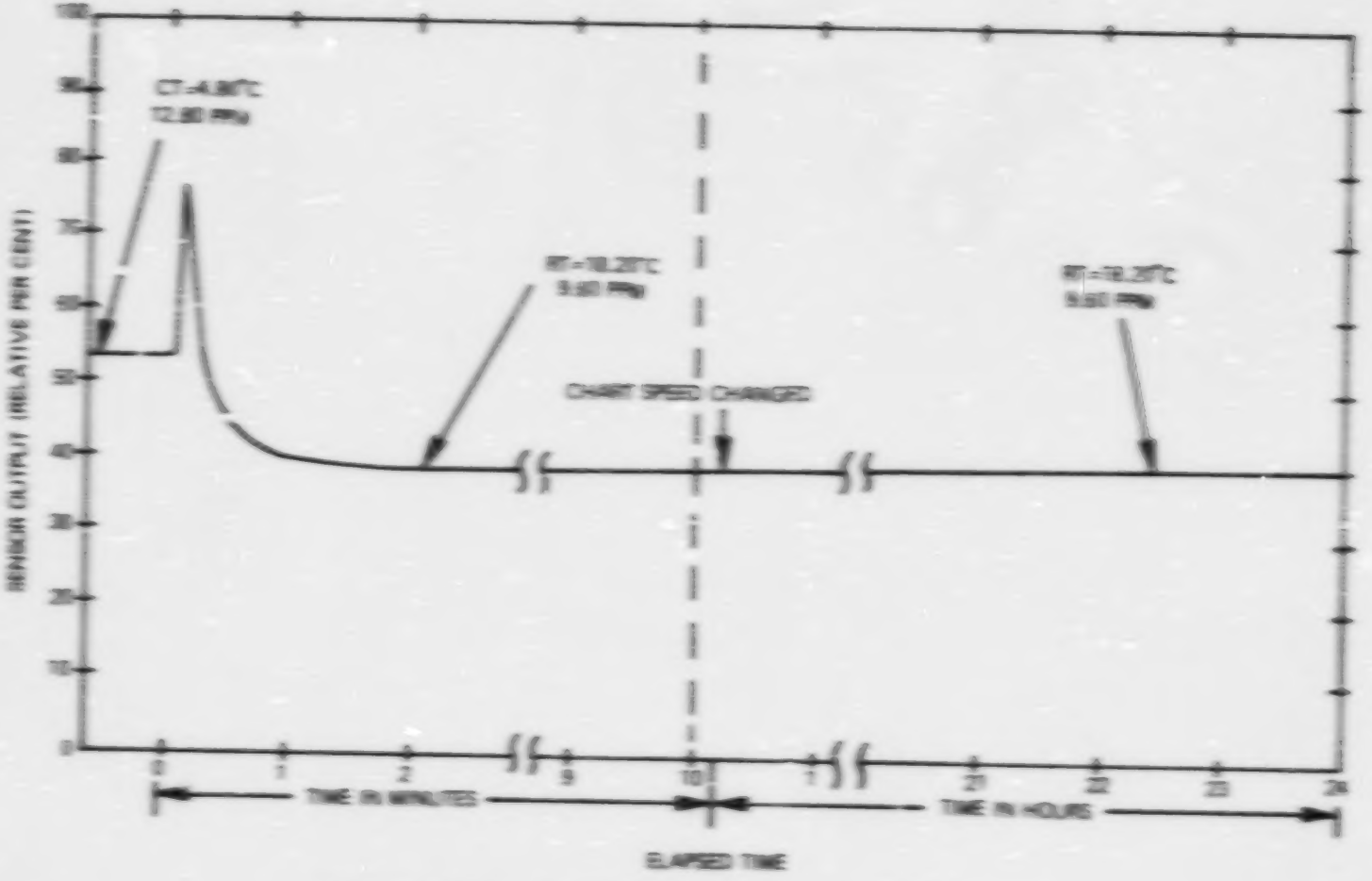


FIGURE 16. TWENTY-FOUR HOUR TOTAL SENSOR RESPONSE (CT-87).

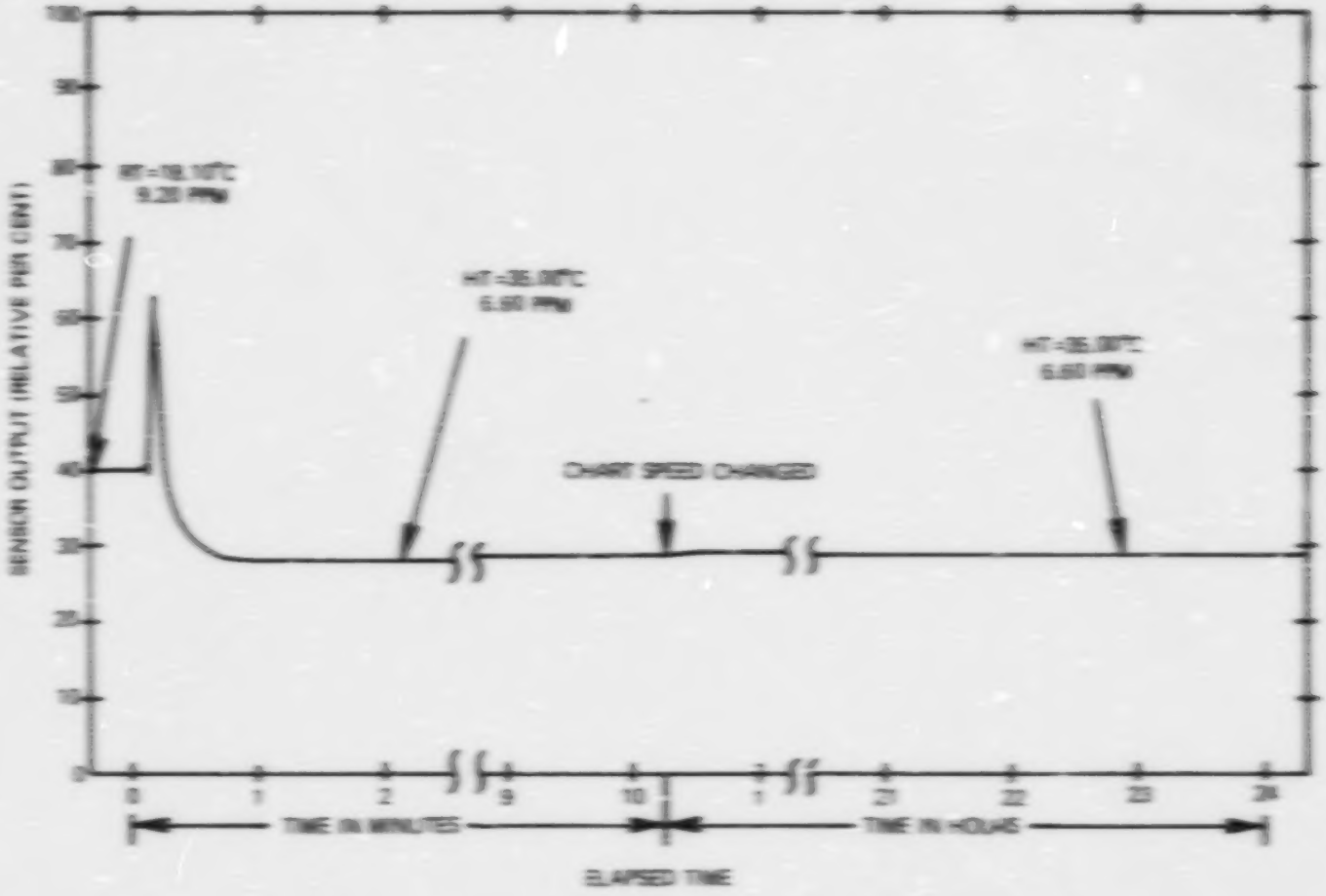


FIGURE 12. TWENTY-FOUR HOUR TOTAL SENSOR RESPONSE (BY-HT).

cathode and generated a higher output current. As the thermistor approached the higher temperature, its reduced resistance produced a lower output potential from the DO sensor.

During the transient-response tests, the sensor performed erratically when the HT-RT run was attempted, which indicated that it needed to be reconditioned. This proved impossible to do, however, because the retaining nut on the stem of the cathode could not be loosened and the pressure diaphragm in the electrolyte was not removed out of fear of tearing it. However, the electrolyte was exchanged and much of the accumulation drained from the sensor. Contrast between the new and old electrolyte can be seen in Figure 18.

The diaphragm was tested to determine its impedance by employing electrolyte on both sides. The results was satisfactory--the impedance was 10 megohms.

After exchange of electrolyte and membrane, the output varied several percent for similar conditions and is consistent with the variations suggested by Figure A-1 in the Appendices.

After the sensor was partially reconditioned, an acceptable RT-HT response was obtained but the reverse run was unsatisfactory because the "O" ring had been improperly seated and water leaked into the electronic compartment of the sensor head (Figure 19).

Uncompensated Sensor - Honeywell provided a replacement plug without diaphragm so that the investigation of the sensor's components could be pursued.

Thus, following sensor maintenance (clean cathode, new electrolyte, and new membrane), response data for an uncompensated sensor were obtained. The thermistor was replaced with a fixed resistor whose low-temperature coefficient had previously been verified.

The temperature-compensating potentiometer was bypassed, therefore only the electrochemical and mechanical components were involved. Procedures outlined in Table 5 were followed, and transient data for 10 and 60 minutes and for 24 hours were obtained. Segments of these continuous recordings are shown in Figures 20-23.

The graphs indicate that response times were longest when the sensor was transferred from lower to higher temperatures (note values at break in graph). Table 7 summarizes several pertinent response points. (Note that the output failed to return to initial conditions.)

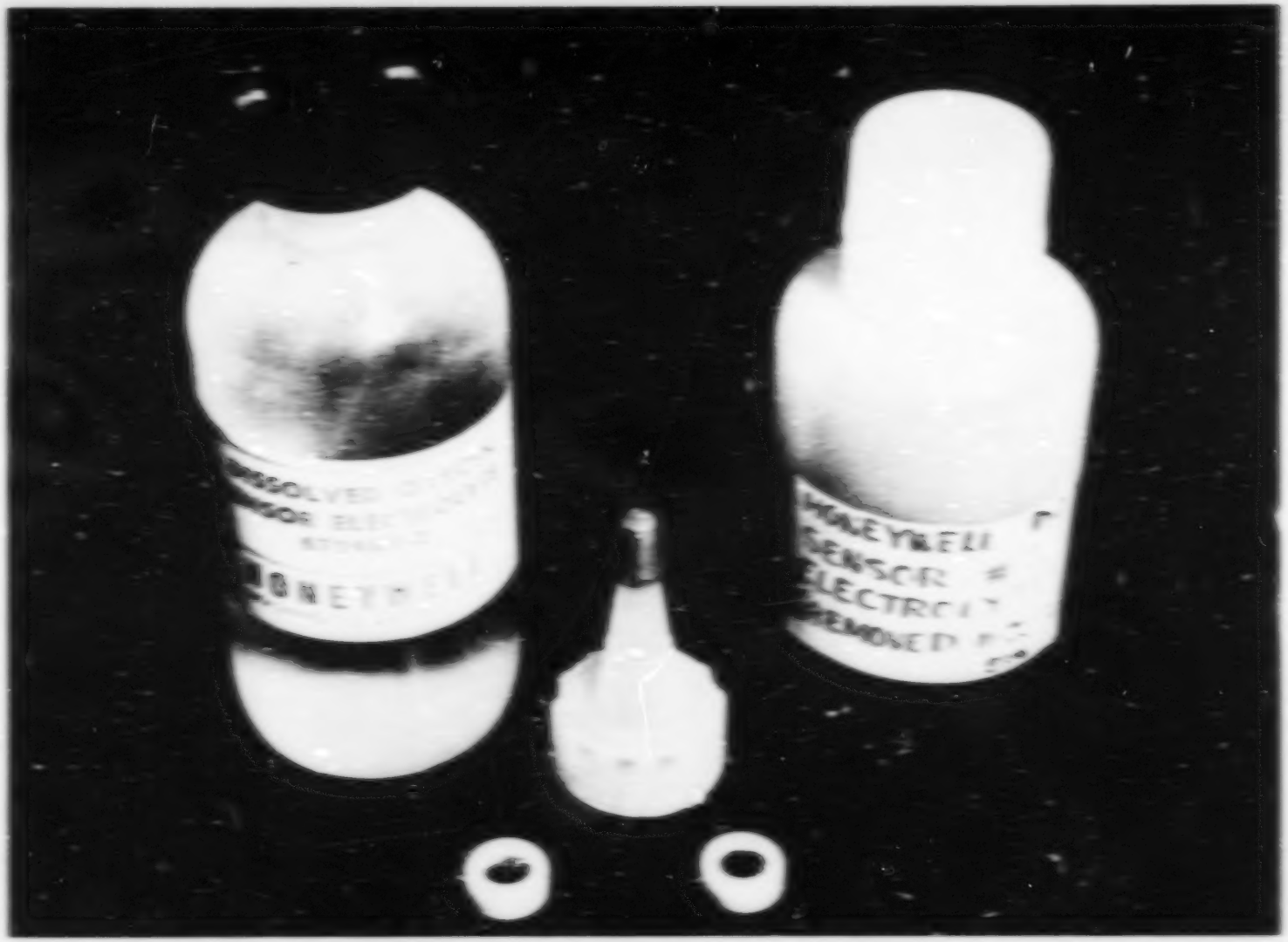


FIGURE 18. NEW AND OLD ELECTROLYTES.

FIGURE 19. SENSOR HEAD.

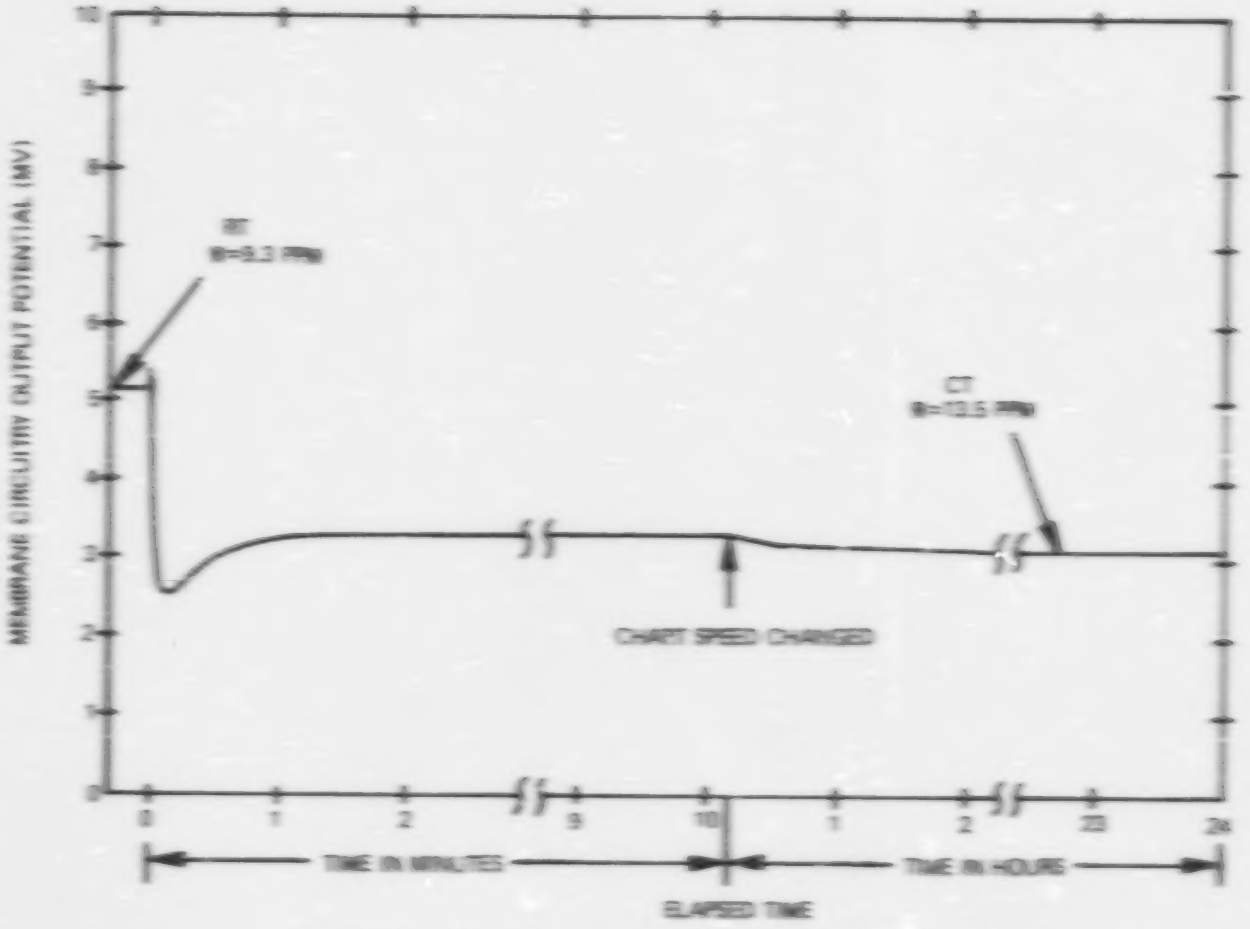


FIGURE 38. TWENTY-FOUR HOUR MEMBRANE RESPONSE (RT-CT).

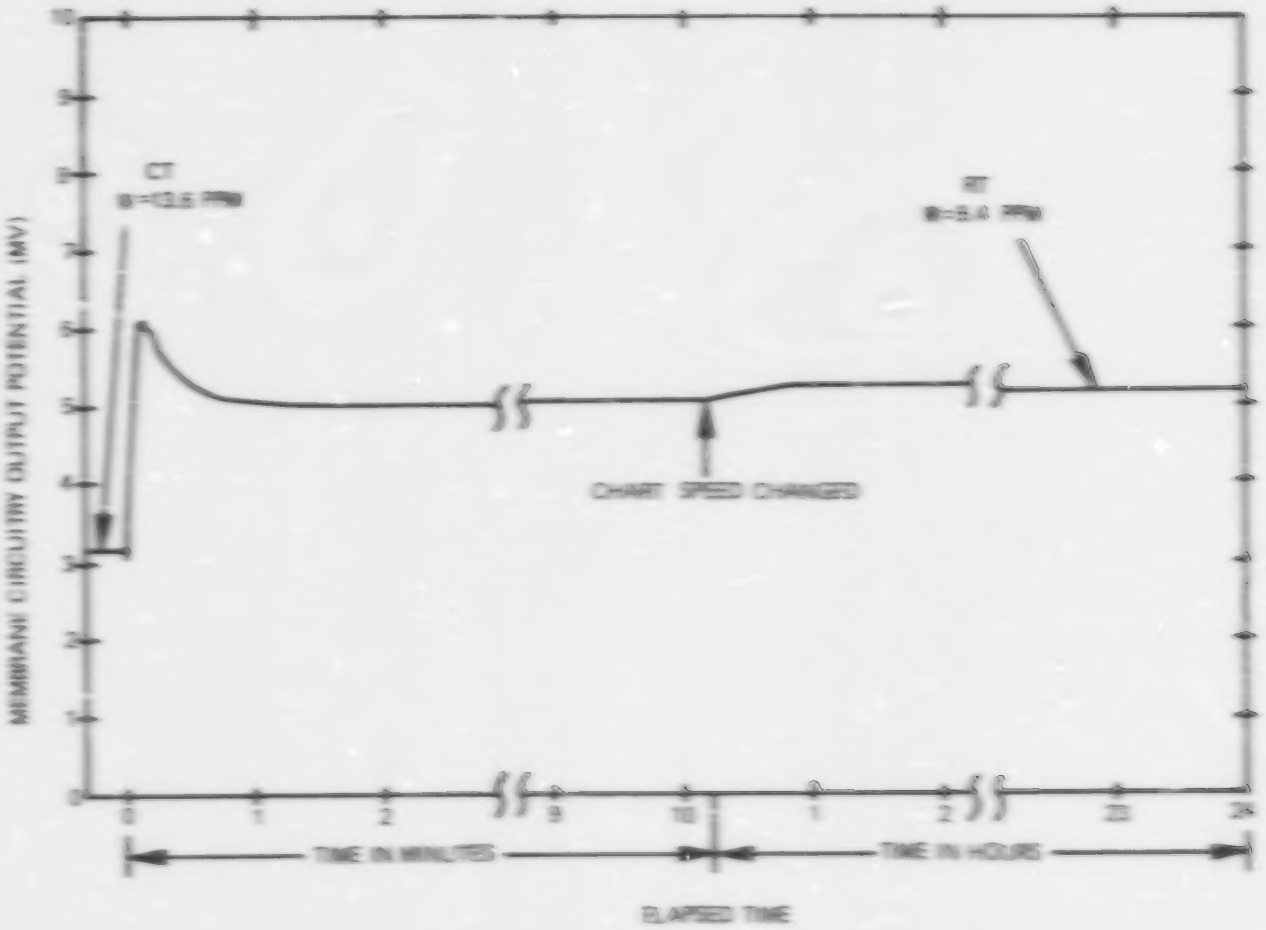


FIGURE 21. TWENTY-FOUR HOUR MEMBRANE RESPONSE (CT-RT).

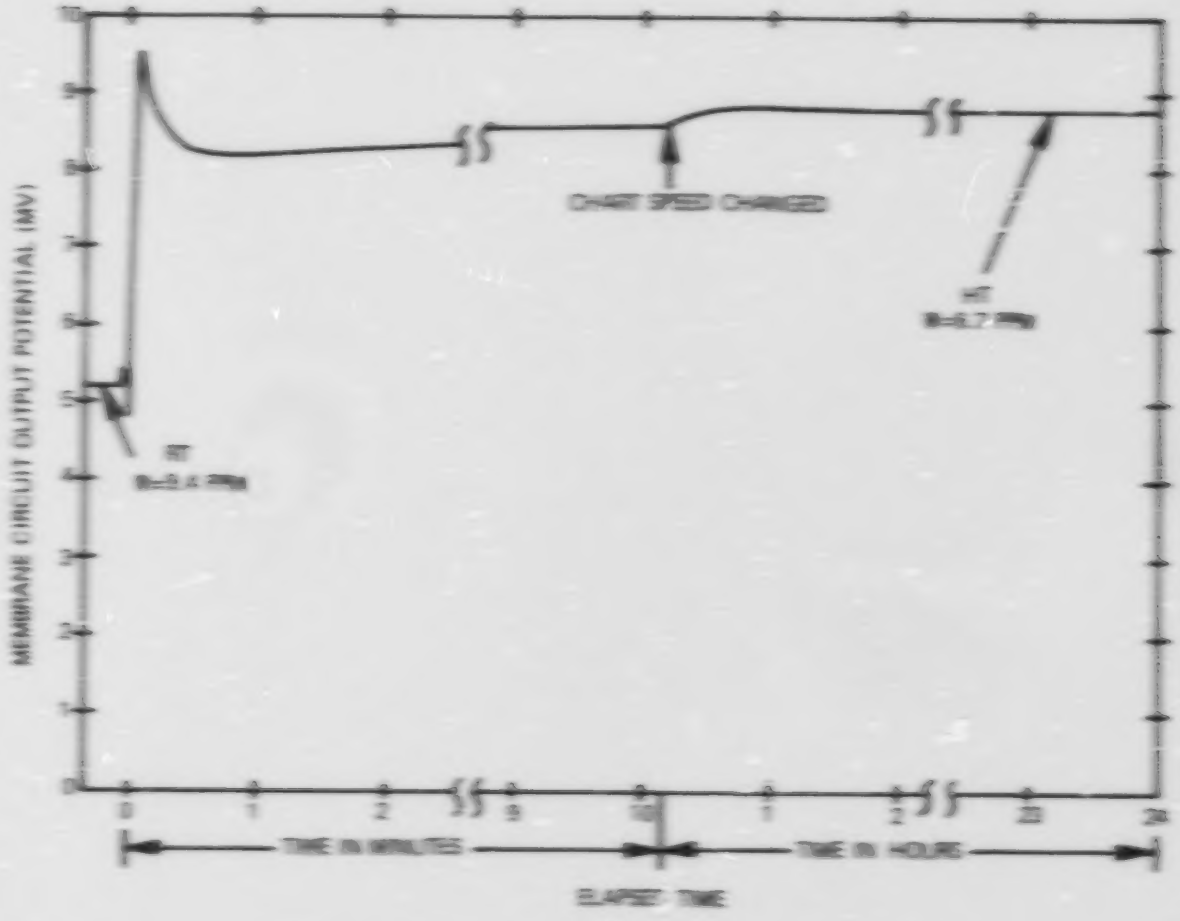


FIGURE 22. TWENTY-FOUR HOUR MEMBRANE RESPONSE (87-47).

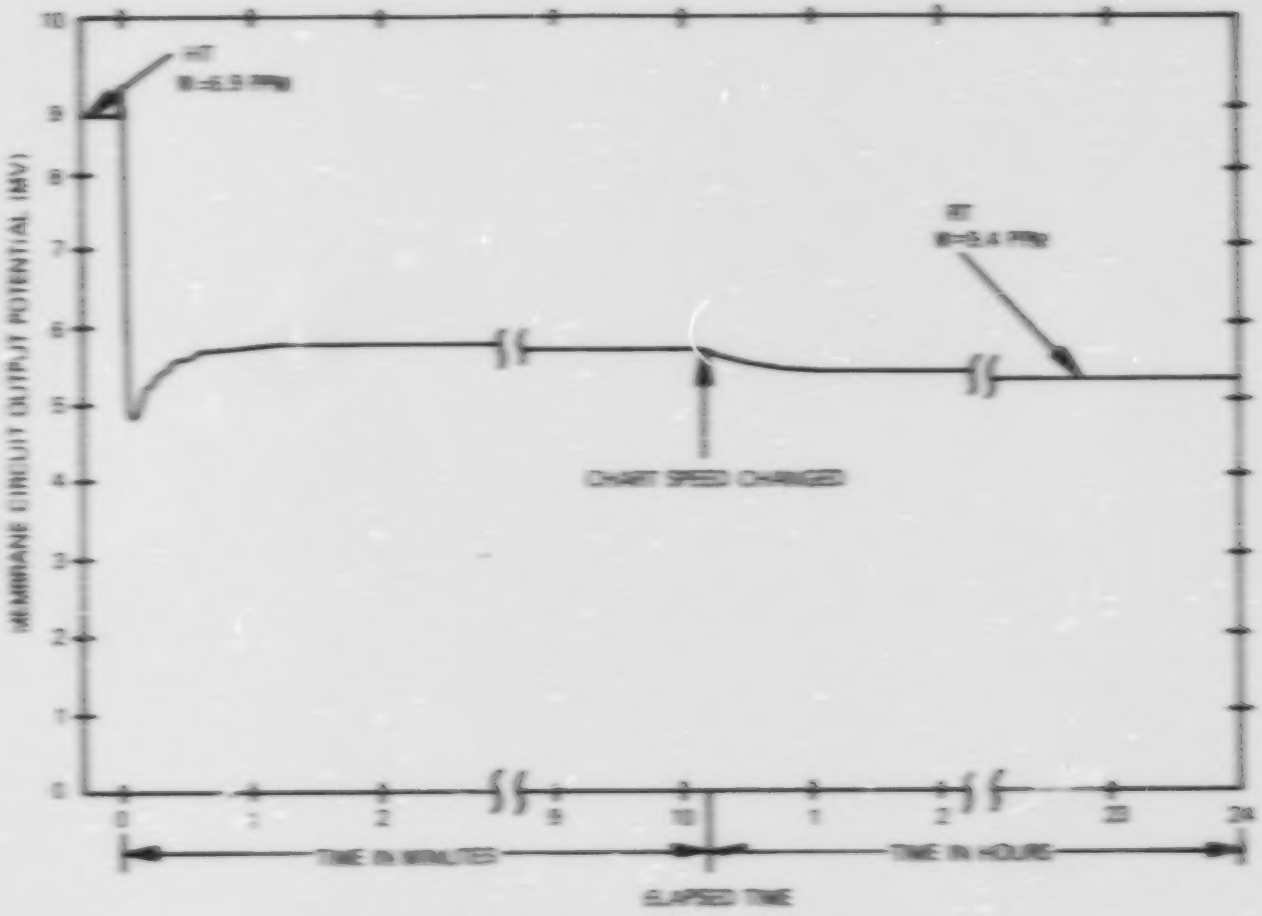


FIGURE 23. TWENTY-FOUR HOUR MEMBRANE RESPONSE (HT-HT).

Table 7. SELECTED RESPONSE POINTS FOR MEMBRANE ONLY

Transfer	Minutes 0	2	10	Hours 2	24
	Amplitude, %			Amplitude, %	
RT→CT	52.0	35.5	35.7	52.0	51.0
CT→RT	52.0	50.0	50.0	55.0	52.0
RT→HT	52.0	85.0	86.0	89.0	87.5
HT→RT	88.0	58.0	52.5	54.0	53.0

RT = 18.3C W_{RT} = 9.3
CT = 1.7C W_{CT} = 13.5
HT = 35.0C W_{HT} = 6.5
W = Winkler determination of dissolved oxygen.

Thermal Compensator - Response of the thermal compensator was investigated by replacing the sensor with an 8K resistor mounted in the MV/V, and measuring the potential developed across the output network as a function of temperature and time. Response and long-term stability are displayed in Figures 24-27.

Table 8 summarizes the steady-state thermistor resistance for the test temperatures noted.

Table 8. THERMAL COMPENSATOR RESISTANCE

Temperature (C)	Resistance (K)
5.0	2.10
18.6	0.94
35.0	0.38

In concluding the sensor investigations, the cold-bath flow system was replaced because excessive overshoots continued to be recorded. Figure 28 reflects the values obtained after this was done. The data displayed in Figures 29-31 were recorded before the plumbing was corrected but in all cases, the flow was approximately of the same magnitude. The slight overshoots detected were apparently caused by the test set up and the main stream line of flow with respect to the assembly. Regardless, the output was within 98 percent of steady state at 2 minutes, as noted previously.

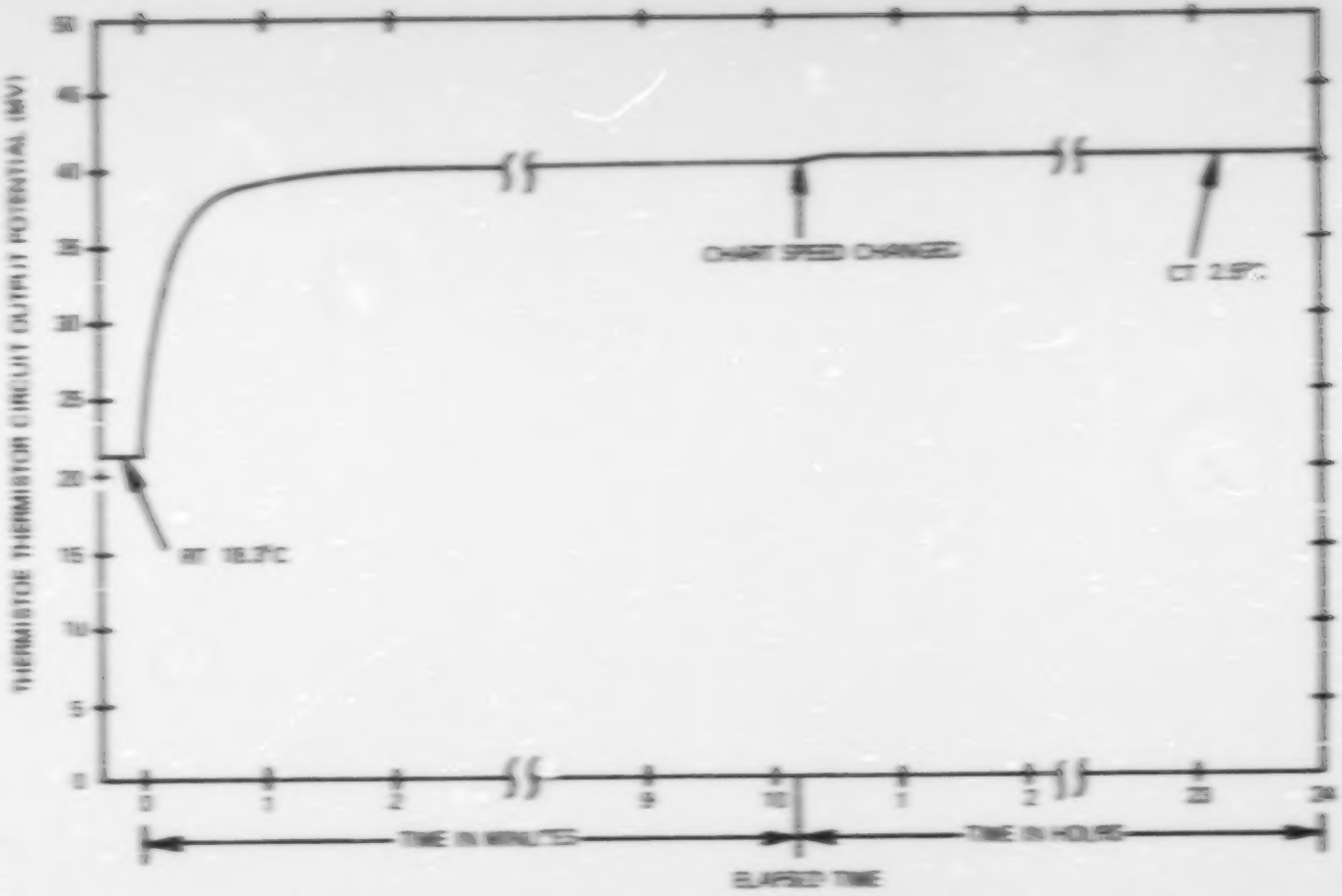


FIGURE 24. TWENTY-FOUR HOUR THERMISTOR DAILY RESPONSE (AT-CT).

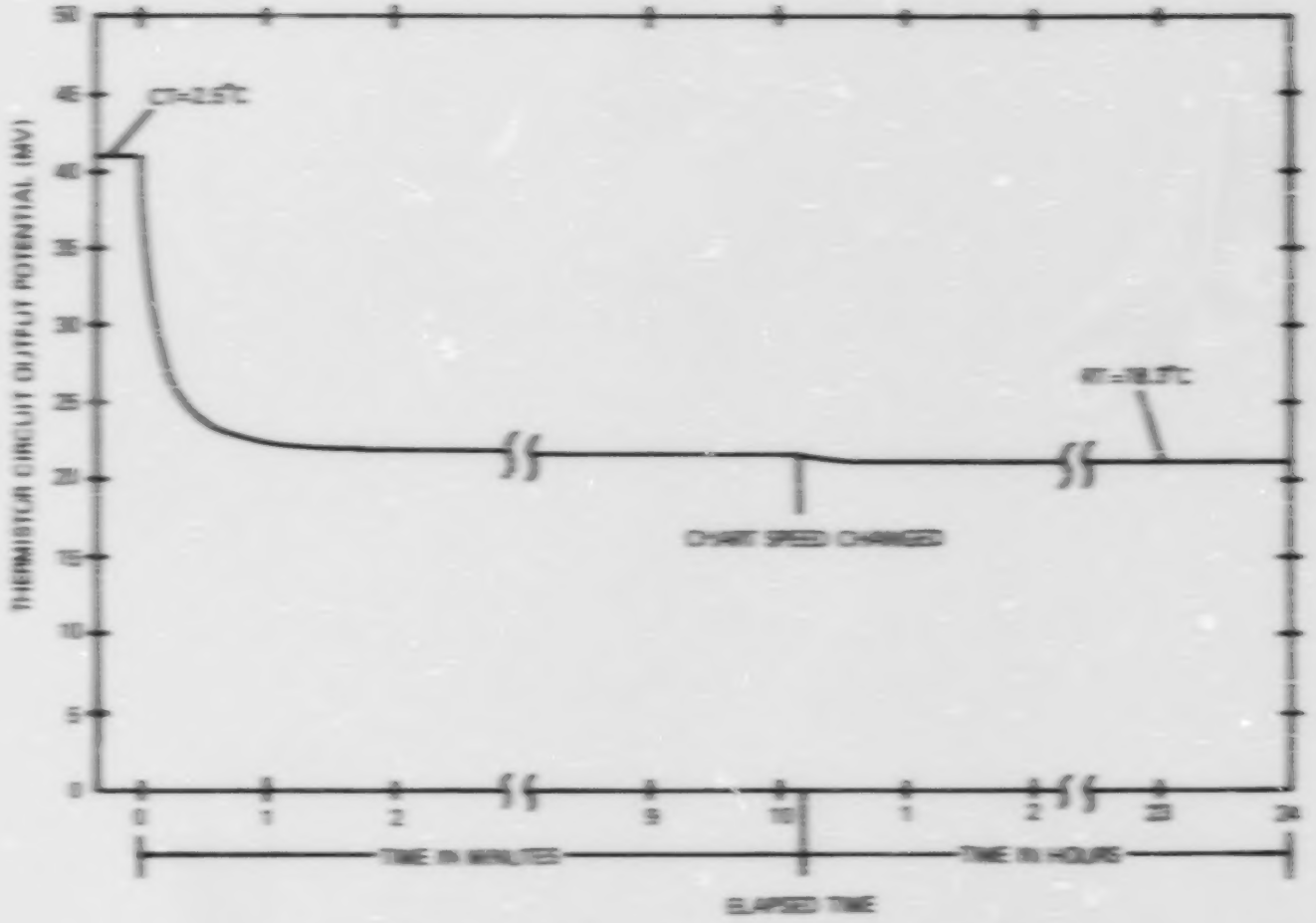


FIGURE 25. TWENTY-FOUR HOUR THERMISTOR ONLY RESPONSE (CT-40).

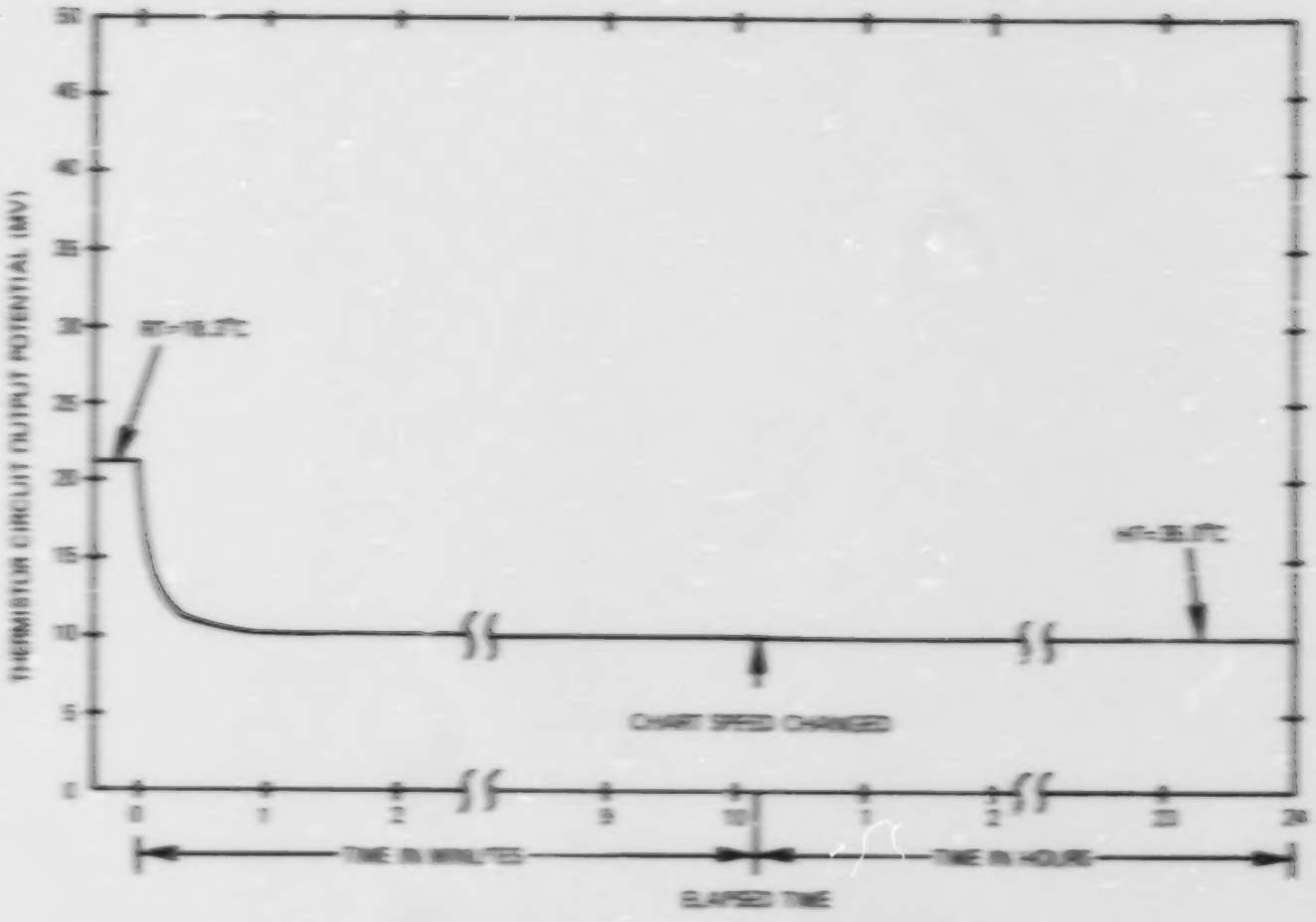


FIGURE 33. TWENTY-FOUR HOUR THERMISTOR RESPONSE (ST-47).

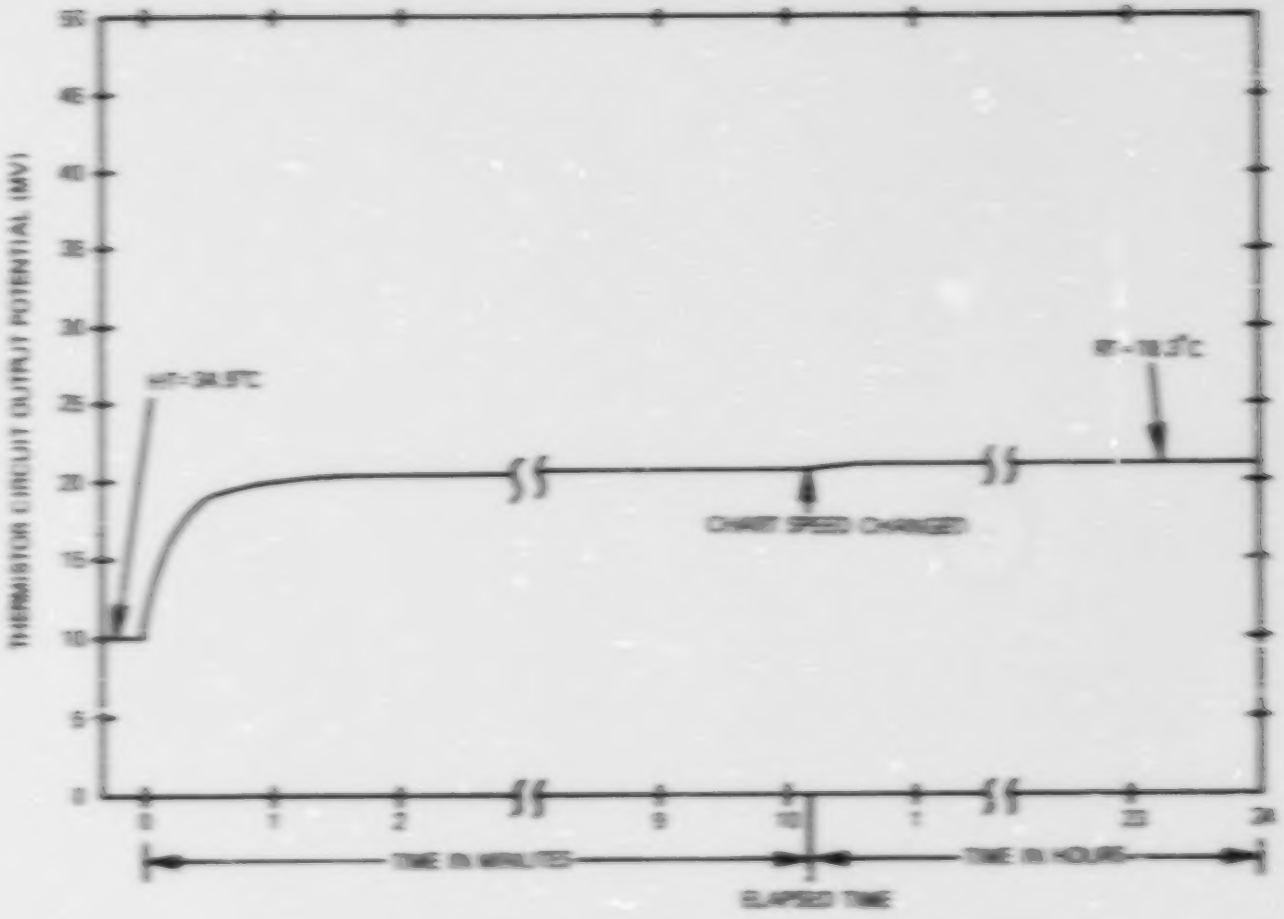


FIGURE 27. TWENTY-FOUR HOUR THERMISTOR ONLY RESPONSE (HT-40).

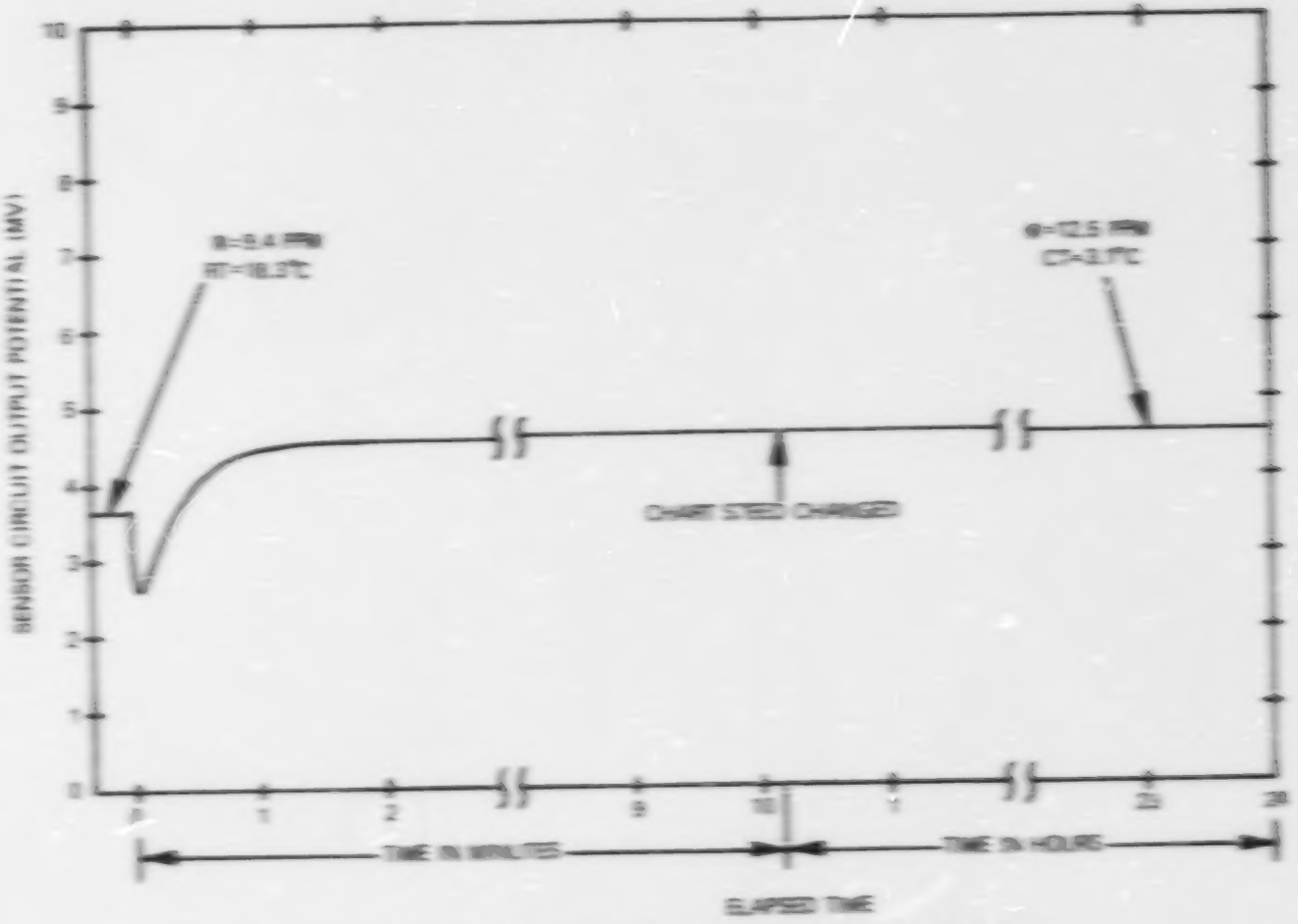


FIGURE 28. TWENTY-FOUR HOUR TOTAL SENSOR RESPONSE (RT-CT).

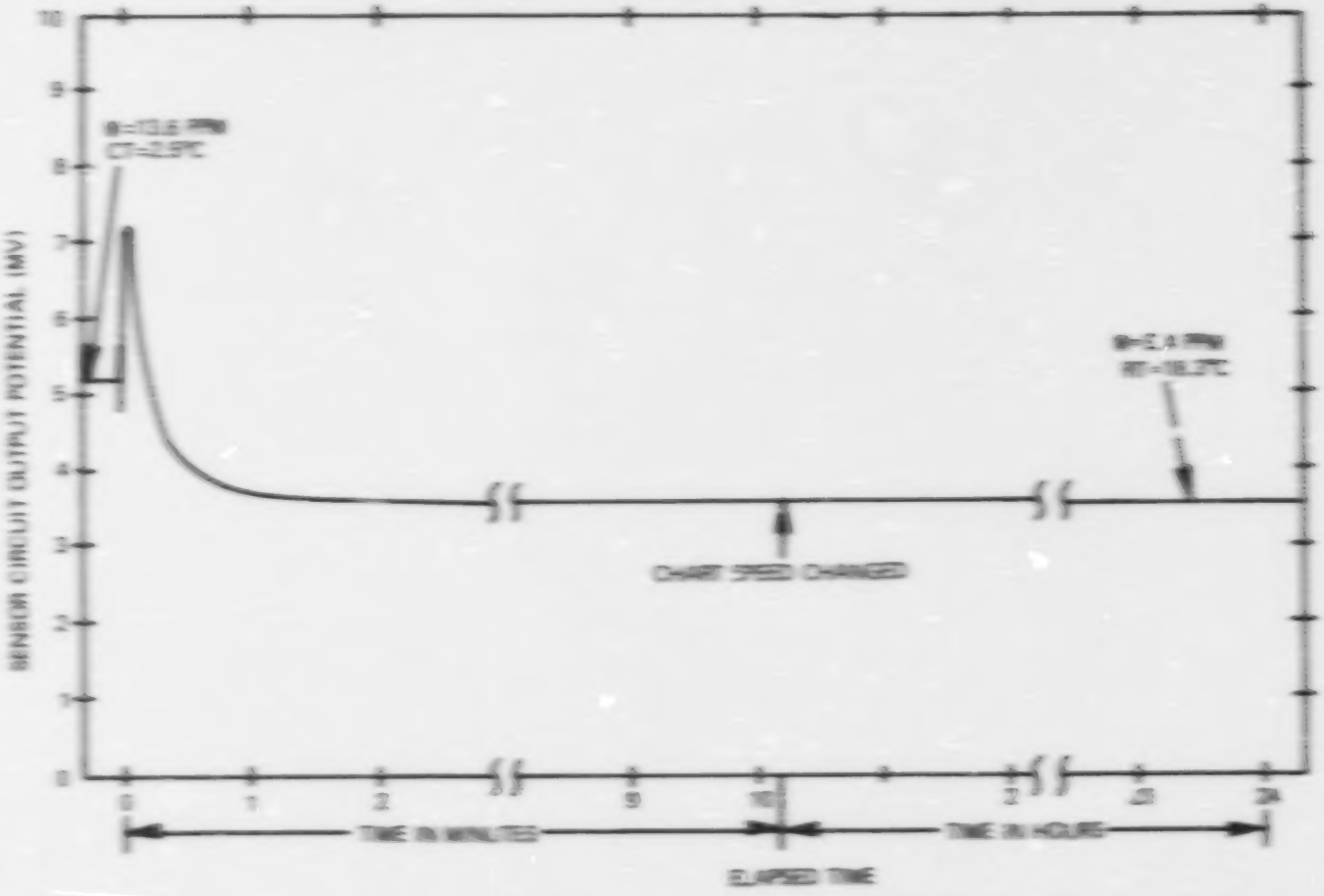


FIGURE 29. TWENTY-FOUR HOUR TOTAL SENSOR RESPONSE (CHR).

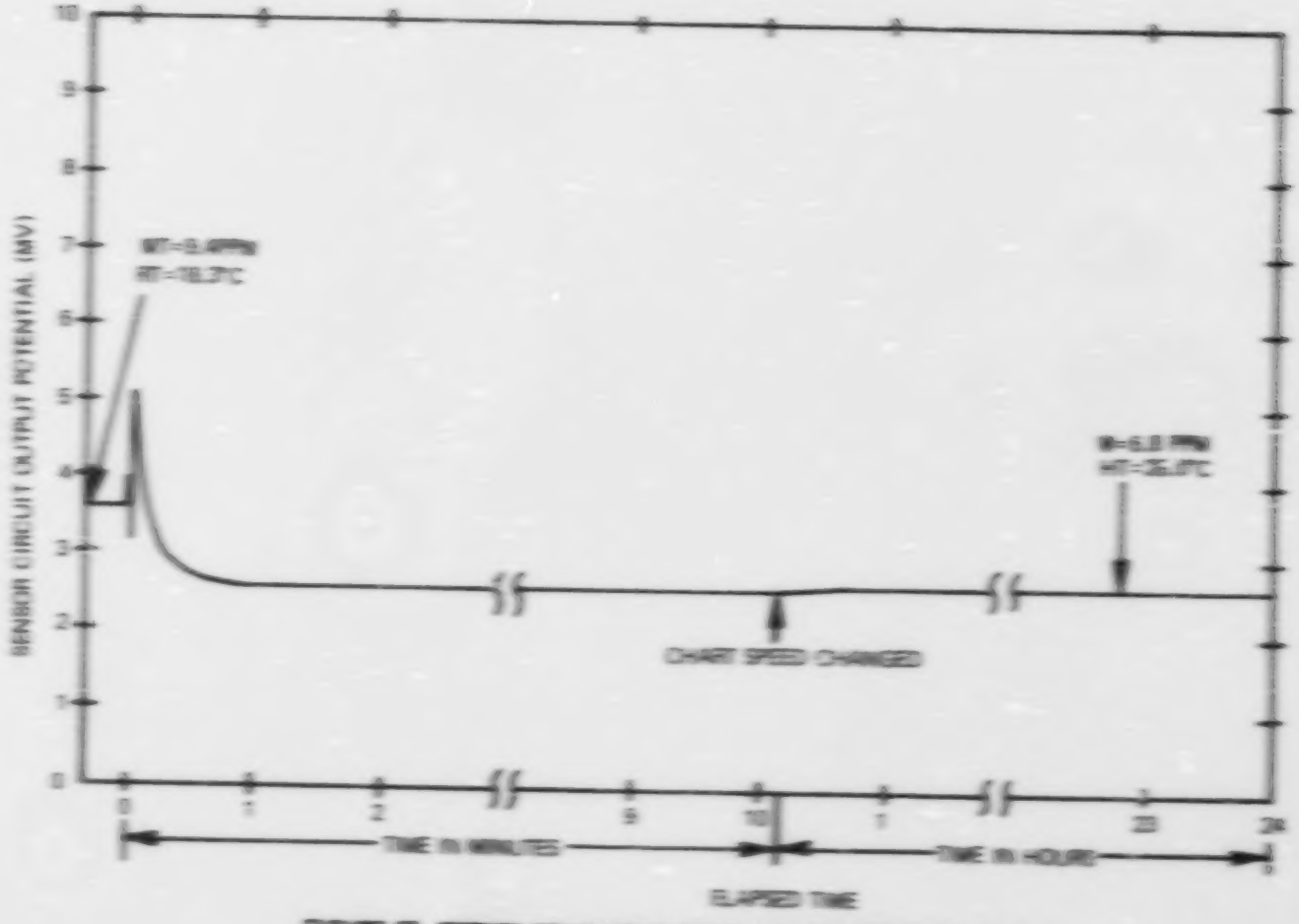


FIGURE 3B. TWENTY-FOUR HOUR TOTAL SENSOR RESPONSE (BF-22).

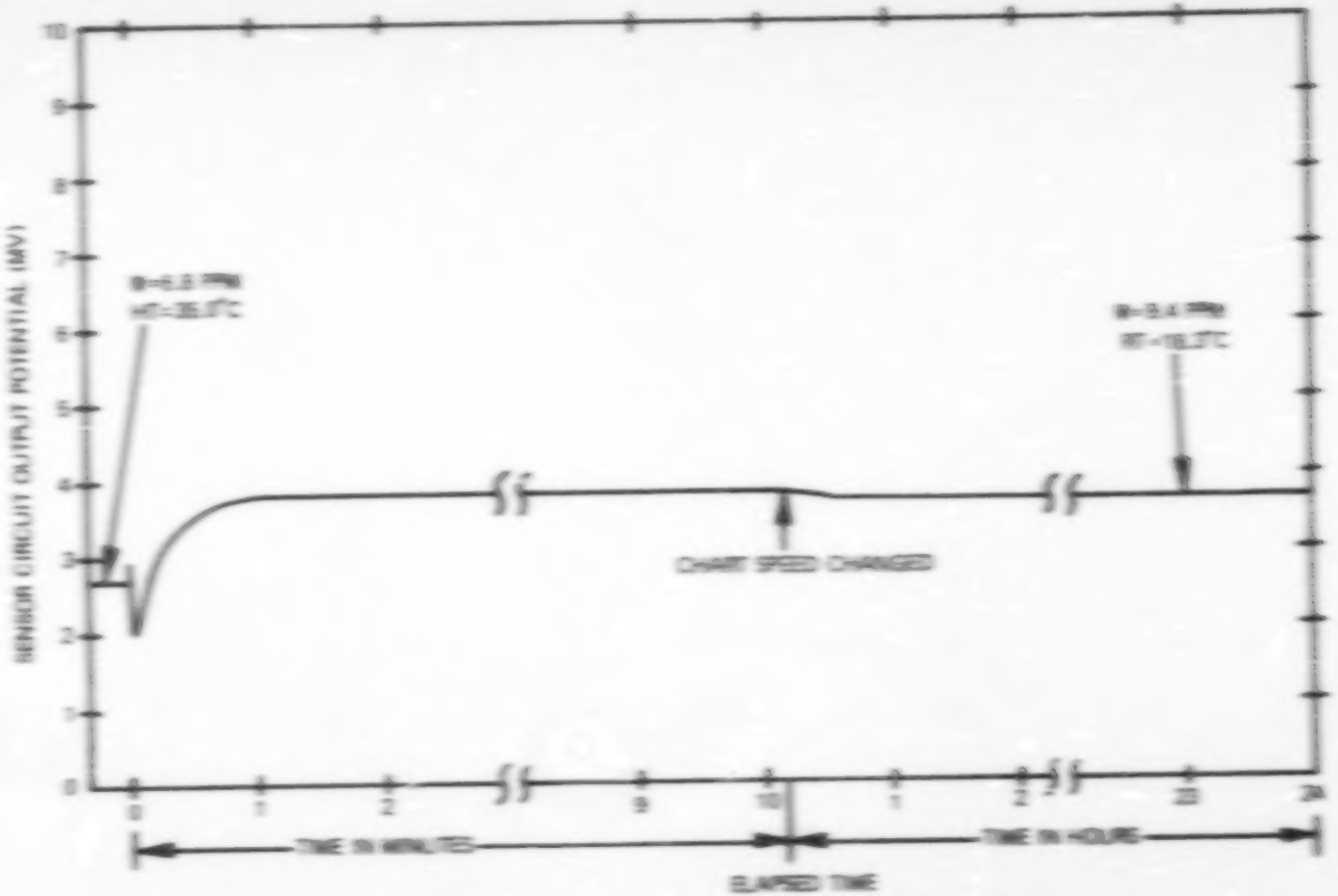


FIGURE 31. TWENTY-FOUR HOUR TOTAL SENSOR RESPONSE (NITRIC

Table 9 summarises Honeywell's specifications for the DO sensor assembly.

Table 9. MANUFACTURER'S SPECIFICATIONS FOR SENSOR ASSEMBLY

Input range -	0-2 to 0-25 mg/l.
Output -	Nominal 0.55 mv/mg/l (±5%).
Output impedance -	3200 ohms maximum at 0C. 190 ohms minimum at 45C.
Accuracy (reference) -	Within 0.1 mg/l or 1.0% of reading (whichever is larger).
Response time -	1 min. maximum to reach 98% of span change step in DO; 2 min. maximum to reach 98% of temperature change step.
Long-term - (30 days)	0-2 mg/l typical maximum.
Normal operating conditions -	Water temperature: 0 to 45C; compensation adjustable to within 0.10 mg/l over entire temperature range. Air temperature: 0 to 45C. Relative humidity: 0 to 100% less than ±0.25% of reading effect for any combination of temperature and humidity. Polarising power supply: 0.8 volts DC ±0.1 volt. Sample/flow velocity: Any constant velocity (±20% from 1.5 to 11 fps).
Operative limits -	Water temperature: 0 to 45C. Air temperature: 0 to 50C. Transportation and storage - air temperature: 5-60C; mechanical shock - 50g for 30 msec.; vibration - 5g over 0 to 60 Hz.
Material specifications -	Electrodes: Gold cathode, silver anode-both immersed in the electrolyte. Electrolyte: 0.5 normal potassium hydroxide and 2.0 normal potassium chloride in distilled water. Cell body: unplasticised PVC. Membrane: teflon. "O" rings: Buna N. Thermistor guard: stainless steel. Membrane cap nut: stainless steel.

Table 9. MANUFACTURER'S SPECIFICATIONS FOR DO SENSOR ASSEMBLY (continued)

Physical data -	Connecting cable. The self-powered tank type is 24 in. long and terminates in a Cannon XLR-3-12c connector. The remote-powered tank type is 24 in. long and terminates in a MS3106E-14S-2P connector. The submersible type is 50 ft. long and terminates in a MS3106E-14S-2P. Extension cable is available. Weight: tank type 2.5 lb. (1.14 kg). Submersible type: 3.5 lb. (1.50 kg).

MV/V INVESTIGATION

Operational performance of the MV/V transmitter was investigated in the laboratory at selected temperatures for:

1. stability
2. linearity
3. response
   (a) step input
   (b) frequency

to determine whether it met certain items of the manufacturer's specifications listed in Table 10.

The temperature stability was investigated to establish the most favorable environment for operating the MV/V, i.e., under controlled ambient conditions, or in an unheated, steel-roofed shelter in which the ambient temperature would normally follow the outside ambient temperature (0C to 40C). The linearity, which would indicate whether the output would be directly proportional to the DO concentration was determined before and after the field investigation. This would also verify equation 11 in Section IV (MV/V Overview).

The response was determined experimentally by two methods: a sudden input following shorted input terminals, and frequency response for selected chopper frequencies.

Table 10. MANUFACTURER'S SPECIFICATIONS FOR MV/V TRANSMITTER

Range -	DO; fixed extended range 0-5 and 0-10 mg/l.
Source impedance	0 to 5000 ohms.
Output -	0-5 volts DC, non-isolated; as specified.
Load impedance -	250 K ohms minimum for 0-5 volts DC output; 0 to 550 ohms maximum for 4-20 ma output.
Accuracy -	±0.25% FS.
Response time -	2.5 sec. to attain 90% FS step change.
Long-term drift - (30 days)	0.25% FS maximum.
Normal operating conditions -	Ambient temperature and relative humidity (RH): ±0.5% FS shift for any combination of -5 to 50C with 0 to 90% RH. Power supply: ±0.01% FS/volt from 110 to 125 VAC, 50 or 60 Hz ±1 Hz.
Operative limits -	Ambient temperature: -30 to 60C. Power supply: 107 to 127 VAC, 50 or 60 Hz ±10%. Vibration: 0.2g for 10 to 60 Hz. Mechanical shock: 5g for 30 msec.
Alarm -	Separate adjustable "hi-Lo" alarm. Contact rating: 5 amperes, 120 VAC and 2.5 amperes, 220 VAC, resistive load. Alarm contacts: Hi - one normally closed or normally open (selectable); lo - one normally closed or normally open (selectable).

Temperature Stability

Temperature stability was investigated at 1.7, 18.3, and 35.0C employing a constant input of 0.65 mv. During the test, control circuits in the environmental chamber failed which caused a temperature runaway shown by Figures 32 and 33. Data displayed by Figure 34 were obtained immediately after this occurred, and the data for temperature interval T_7 were recorded at an uncontrolled ambient of 25C.

For the total stability test, temperatures were measured at several points within the chamber and near the converter's chassis. This data indicated absence of thermal gradients under steady-state conditions.

There is insufficient data to draw a precise conclusion from the transistory runaway data although the runaway offers an opportunity for speculation.

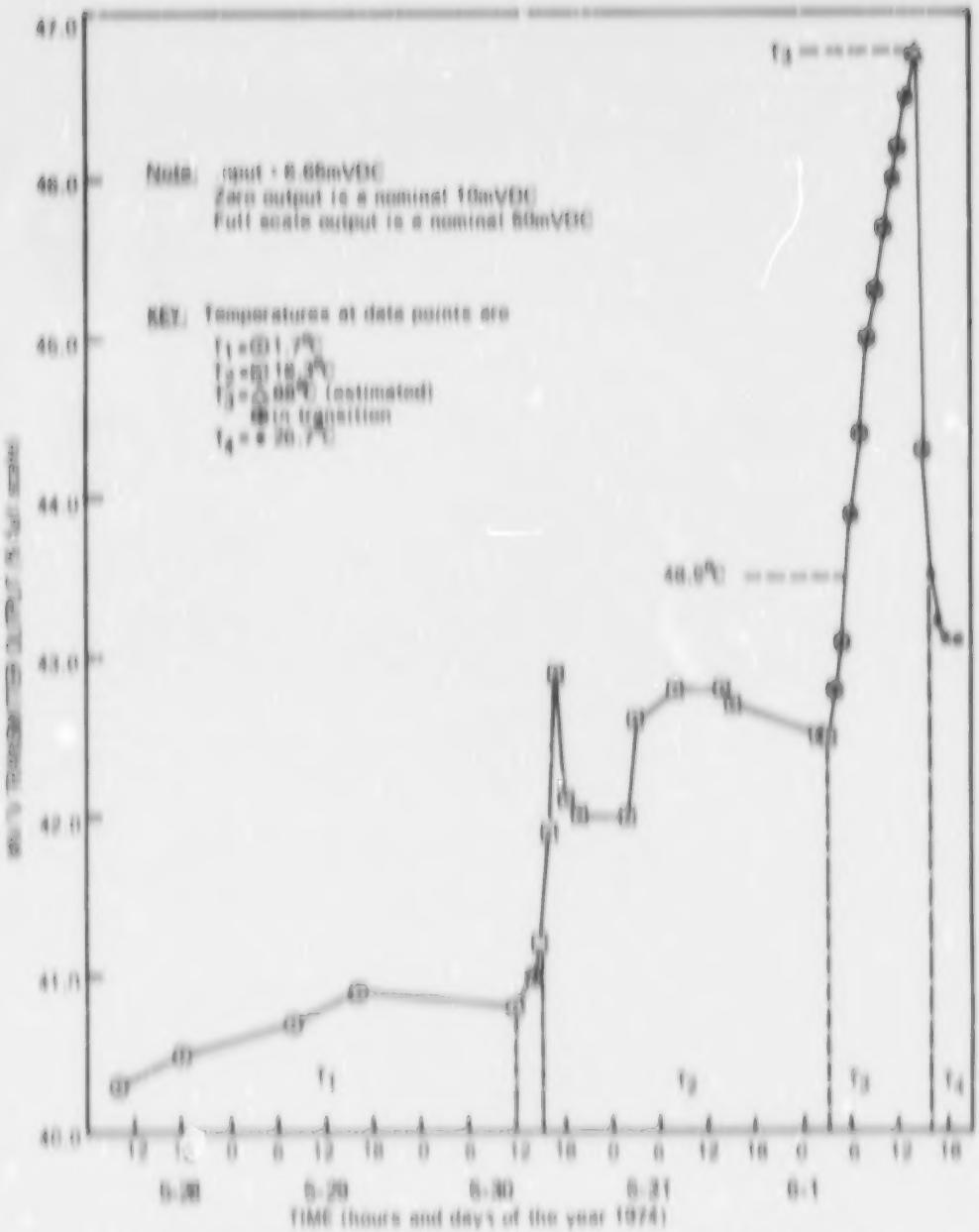


FIGURE 32. TEMPERATURE STABILITY OF MV/V (BEFORE AND DURING RUNAWAY).

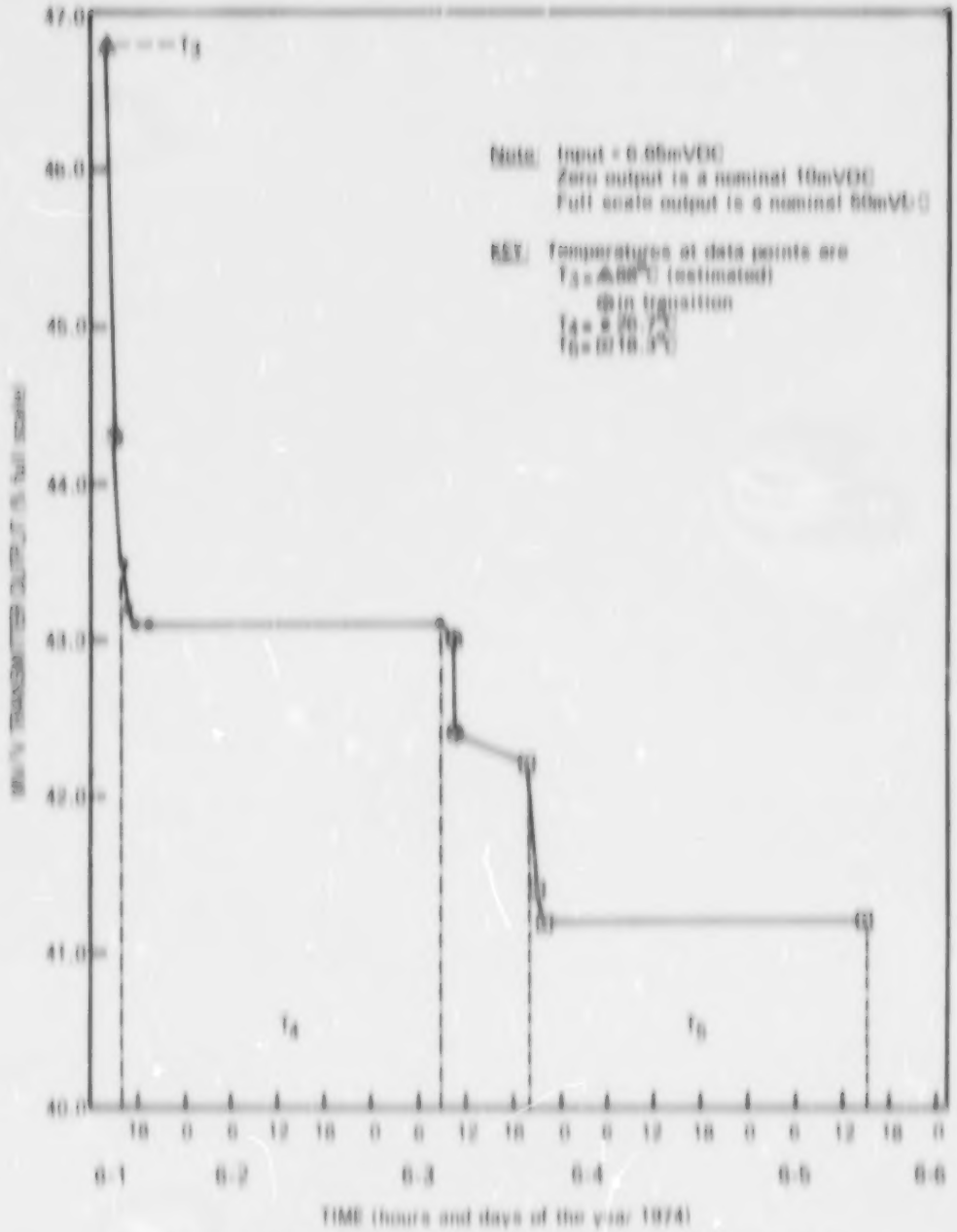


FIGURE 33. TEMPERATURE STABILITY OF MV/V (IMMEDIATELY AFTER RUNAWAY).

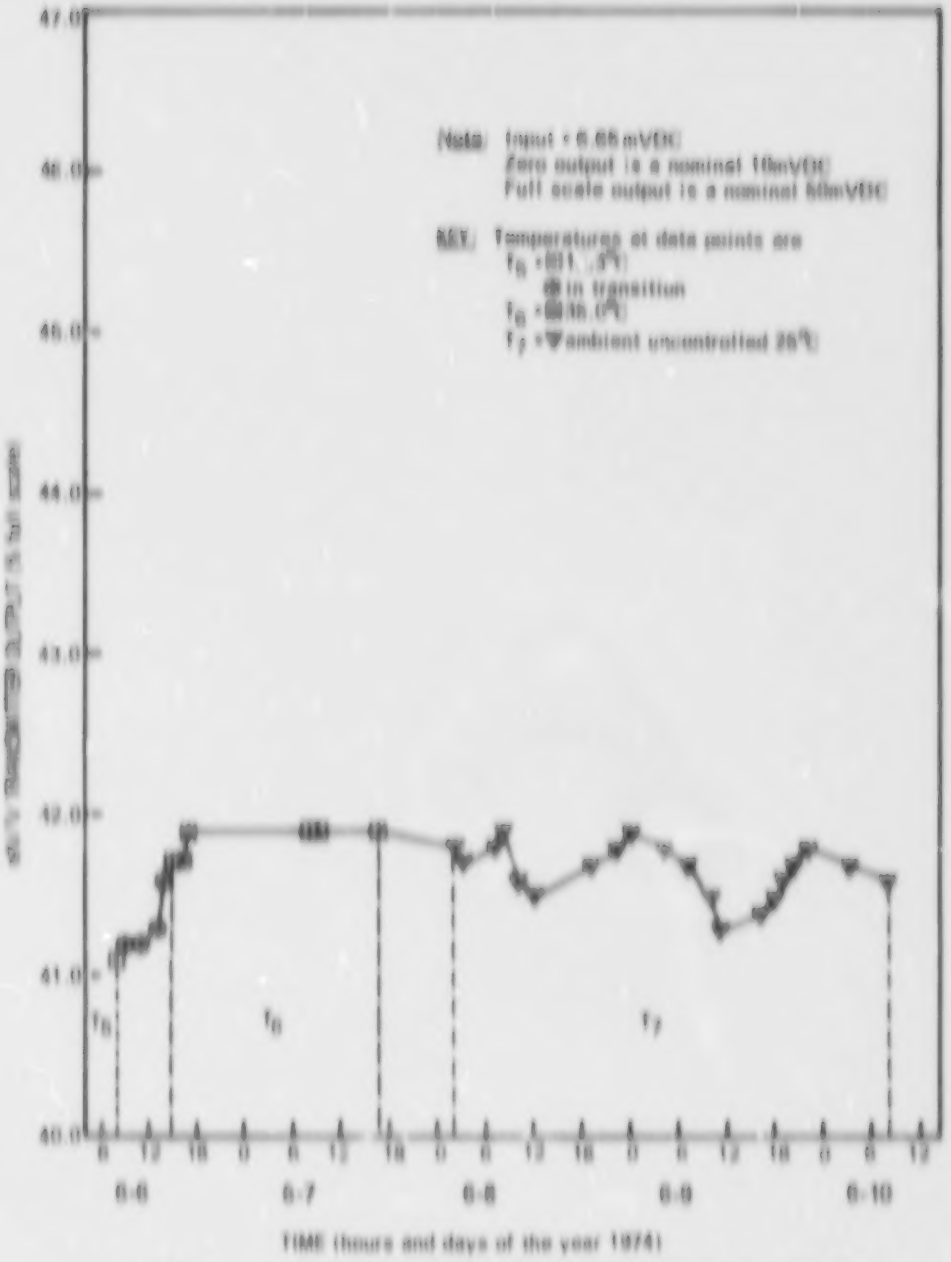


FIGURE 34. TEMPERATURE STABILITY OF MV/V AFTER RUNAWAY.

The data displayed in Figure 32 suggest that the MV/V was temperature-dependent during intervals T_1 and T_2. Change in output at 1.7C (interval T_1) was between 40.5 and 40.9 percent, within ±0.5 percent. At room temperature (interval T_2), the output varied between 41.2 and 42.9 percent for an overall shift of ±0.85 percent. The overall shift for the maximum excursion (worst case) between each interval was 2.6 percent, or ±1.3 percent over both intervals.

Very little can be said regarding the runaway itself since thermal gradients existed throughout the chassis, and a steady-state condition was not reached until the chamber was returned to 26.7C in interval T_4.

In interval T_5, the chamber was returned to a controlled 18.3C temperature, which was maintained for approximately 42 hours. The output remained constant. For temperature intervals T_6 (35C) and T_7 (25C), the output varied between 41.7 percent and 41.9 percent, and 41.5 and 41.9, respectively, and within the expected ±0.5 percent tolerance. The maximum variation between both intervals was 41.5 to 41.9, which was within the expected ±0.5 percent tolerance.

Since Honeywell personnel agreed that the MV/V had not been damaged, other testing was pursued.

One month later, following recalibration, the MV/V was again exposed to temperature-stability tests. Data comparable to those displayed in Figures 30, 33, and 34 were obtained and are presented in Figures 35 and 36. At a constant input, the overall spread (worst case) of the output in the controlled environmental chamber was between a high of 44.0 percent at 35C to a low of 42.2 percent at 1.7C. Thus, the shift was actually ±0.9 percent or ±0.4 percent more than expected, but ±0.5 percent less than before the runaway. (Data contained within the dashed sectors indicate a transition and are excluded from the discussion.)

The one basic difference between the method used to obtain the environmental chamber temperature changes presented in Figures 32 and 33 and Figures 35 and 36 was in the employment of the proportional controller. In the first sequence, the slope is steeper since 100 percent of the heat cycle was added, whereas a nominal 50 percent of the heat cycle was employed in the second sequence. The reason for the reduced thermal shift in the output after the runaway was not investigated, but it may have been related to semiconductors, capacitors, or the circuitry and its power supply. The measuring circuit is shown in Figure 37, and Table II summarizes the mid-point output for each temperature interval. (Since the analyzer was "recalibrated" to obtain the data in Part II, there is not equivalence with Part I.)

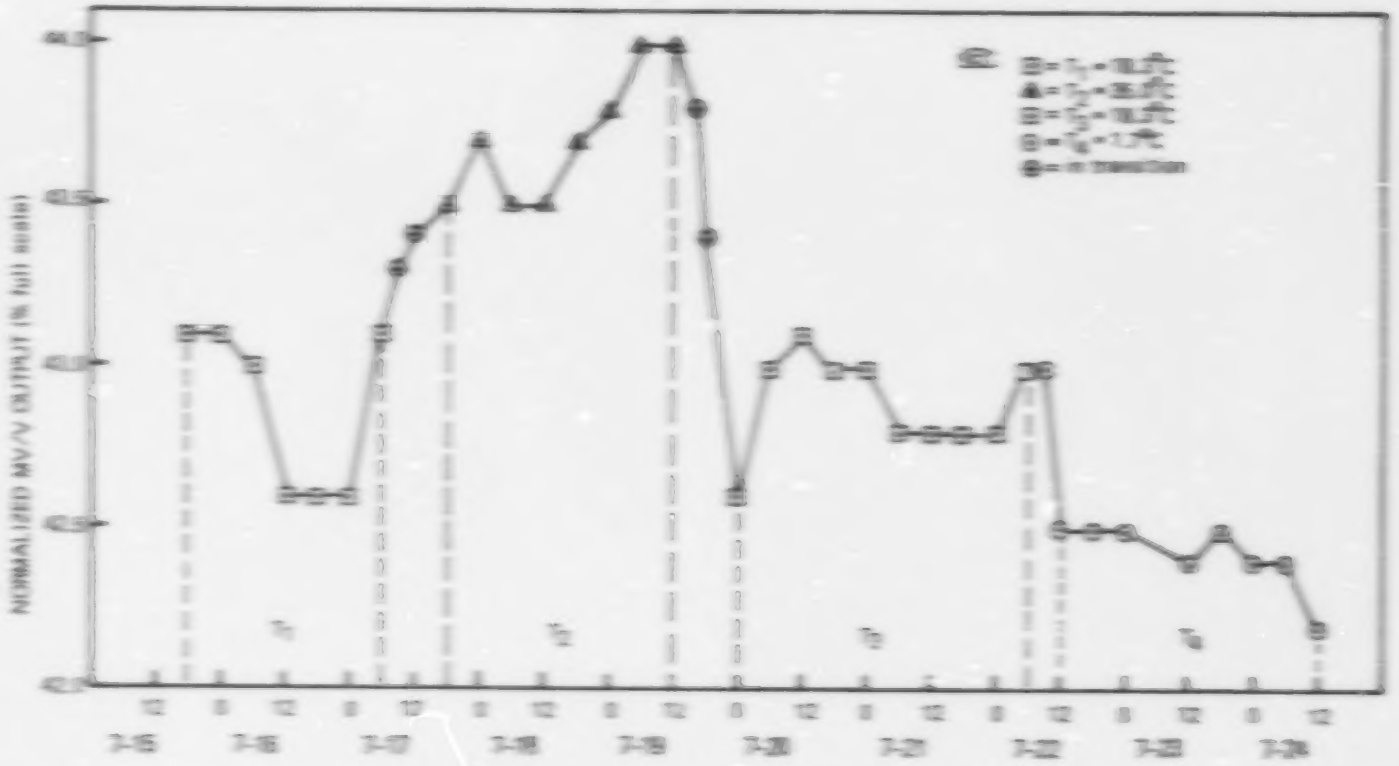


FIGURE 33. TEMPERATURE STABILITY OF MV V (1 MONTH AFTER BONDING).

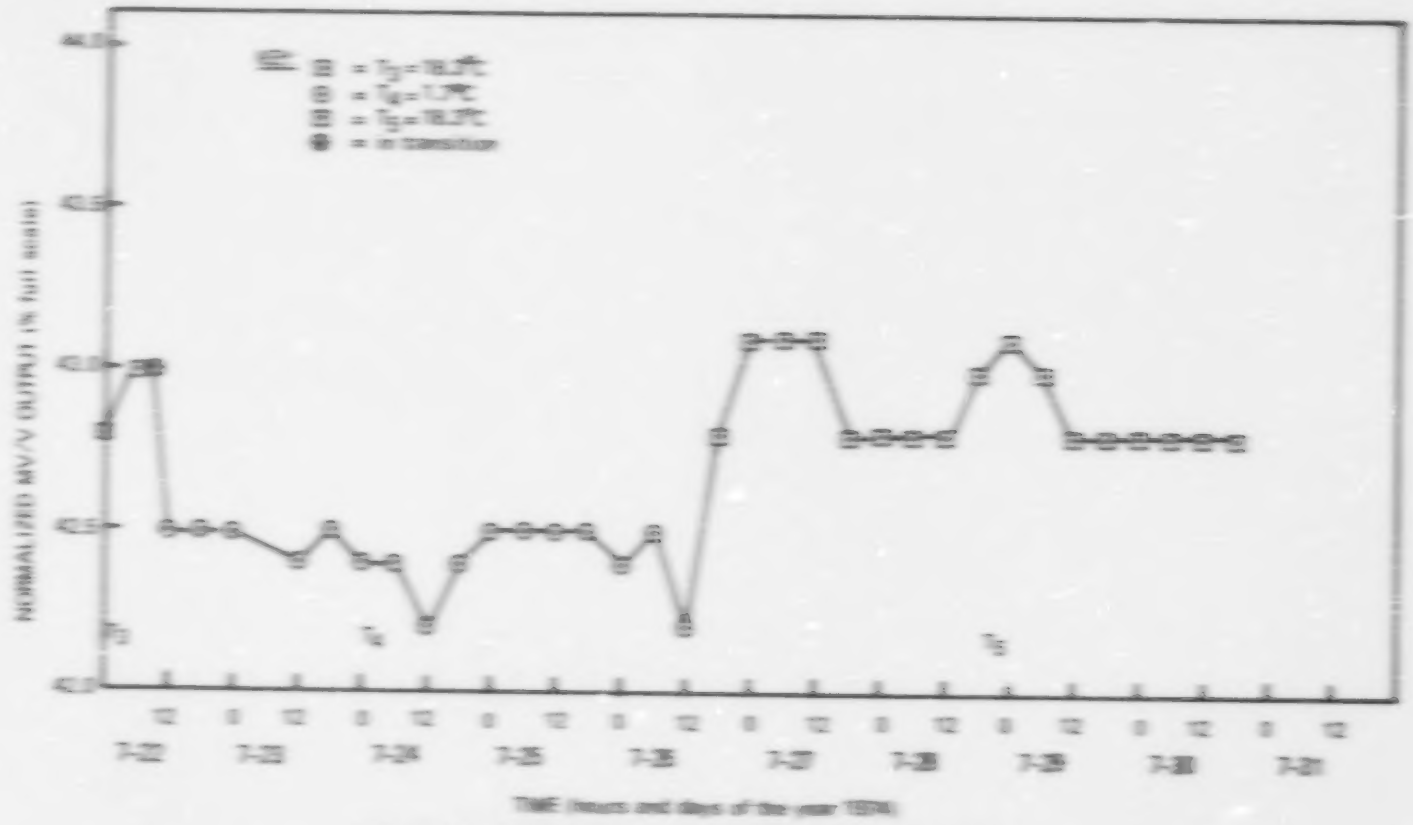


FIGURE 38. TEMPERATURE STABILITY OF MV/V (1 MONTH AFTER RUNAWAY).

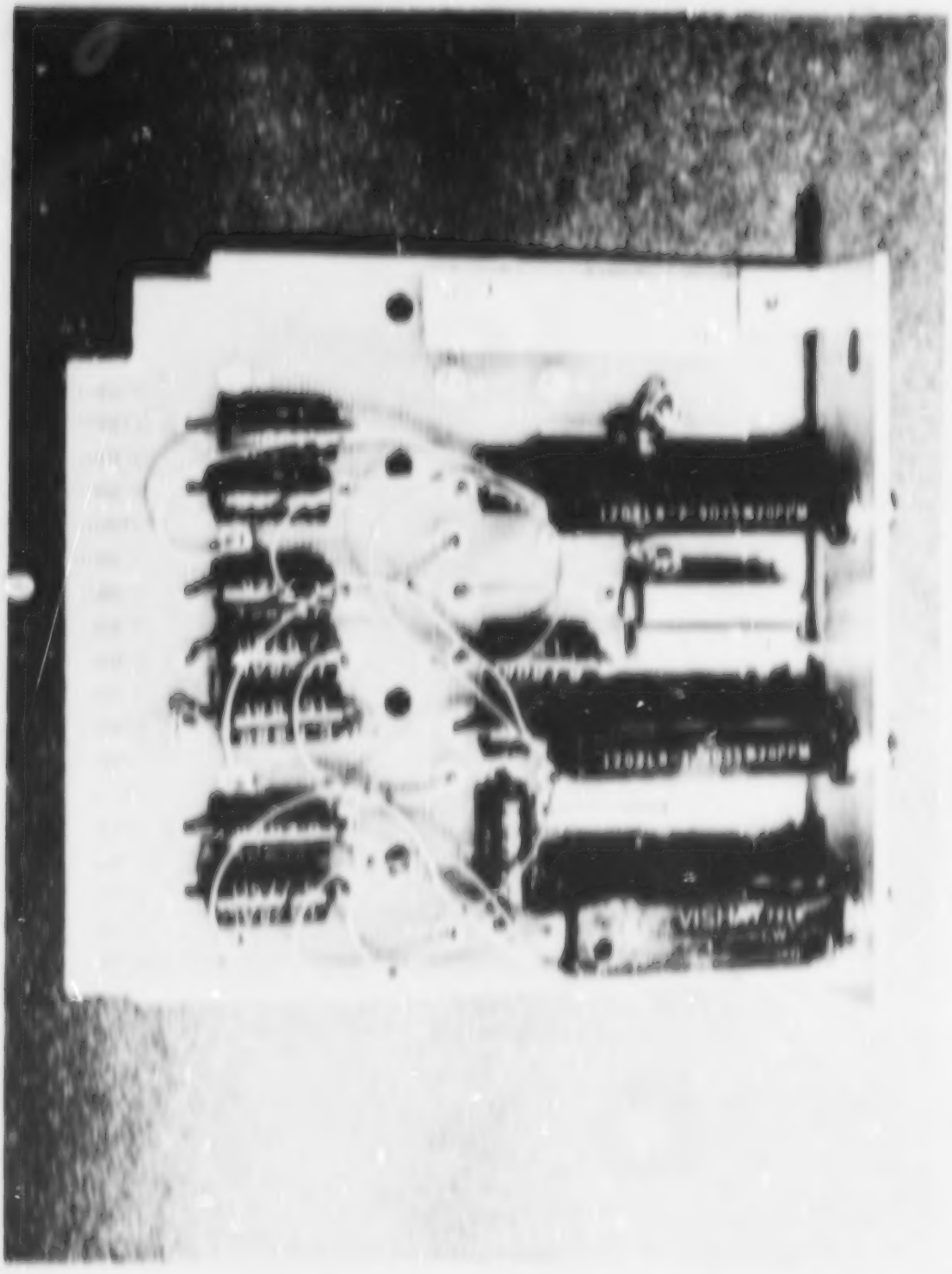


FIGURE 37. MEASURING CIRCUIT COMPONENTS OF MV/V.

Table 11. MV/V THERMAL SHIFT

Runaway	Temperature C	Interval	Duration hours	Output range %	Output mid-point %
Part I					
1. before	1.7	T_1	48	40.5-40.9	40.6
2. before	18.3	T_2	55	41.2-42.5	42.3
3. after	20.7	T_4	24	43.1-43.5	43.3
4. after	18.3	T_5	42	41.2-42.2	41.4
5. after	35.0	T_6	27	41.7-41.9	41.8
6. after	25.0	T_7	54	41.5-41.9	41.7
Part II					
7. after	18.3	T_1	36	42.6-43.1	42.9
8. after	35.0	T_2	48	43.5-44.0	43.7
9. after	18.3	T_3	51	42.6-43.1	42.9
10. after	1.7	T_4	93	42.2-42.5	42.4
11. after	18.3	T_5	90	42.8-43.1	42.9

Linearity

Before the field work was carried out, end-point linearity[7] data for the high range of the MV/V were obtained at 41F, 65F, and 95F (1.7C, 18.3C, 35.0C) (Figure 38). The data were obtained by exposing the MV/V to controlled temperatures in the environmental chamber and employing a Fluke Model 341A voltage source. The input and output (output measured between TP-1 and TP-2) were measured by a Keithley Model 616 digital electrometer. The input was limited to a maximum of 8.0 mv, the equivalent of approximately a 14.5 mg/l DO concentration, and within the expected range of operation.

The data in Figure 38 indicate that the end-point linearity for each temperature was within a nominal ±0.5 percent FS, but the spread (gain) at full scale over the temperature range was 3 percent or ±1.5 percent from room temperature. This spread converges to zero for zero input.

Although the input signal was increased by 30 percent, the apparent increase in gain with temperature is consistent with the stability data shown in Figures 32 and 36.

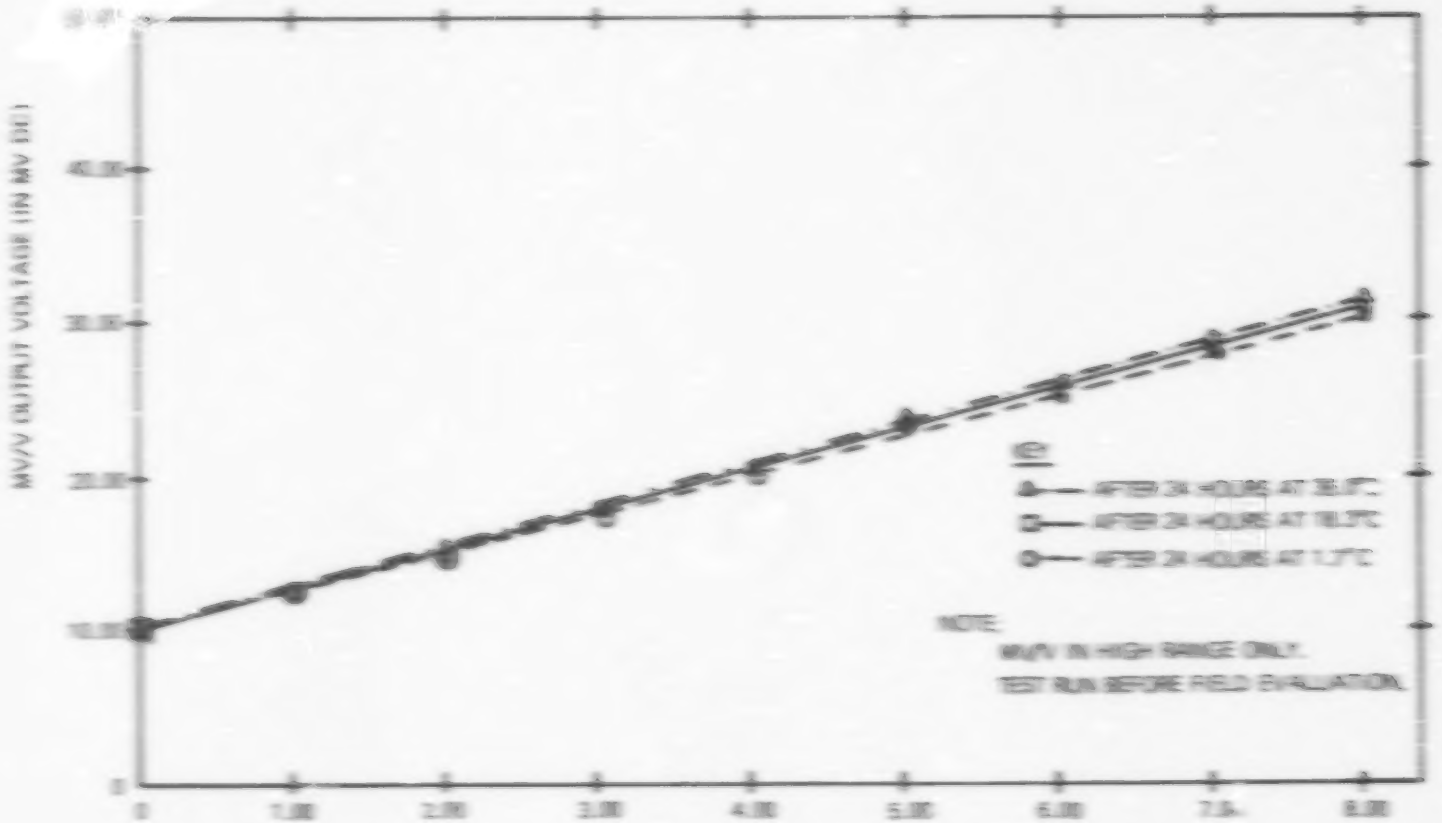


FIGURE 3L MV/V END-POINT LINEARITY.

After the field work was completed, additional linearity data for the potential output and panel meter were obtained to determine what effects, if any, time (approximately 4 months), field calibration, and temperature compensation had had on the unit (Figures 39-41). The MV/V was maintained at 69.8F (21C), and data were obtained for both ranges. The method of investigation was similar to that shown in Figure 38, buy the input range was extended to 14 mv and adjusted to provide panel meter deflections that corresponded to integral markings. The resultant millivolt output and the required input potential were plotted as dependent variables. The independent linearity (output voltage was measured between TP-1 and TP-2) was ±0.5 percent, but the panel meter approached a nominal offset of ±2.5 percent when near zero, and it had a nominal independent linearity of ±1.0 percent.

After the unit was operated in the laboratory for a month, its linearity was again determined for both ranges (Table 12). Except for full scale, the input was adjusted to integral numbers, and the output potential and panel meter deflection were tabulated as dependent variables. (Some meter-reader error may have occurred.)

Table 12. LINEARITY OF MV/V 30 DAYS FOLLOWING INDEPENDENT[a] LINEARITY TESTS

Input Ei (millivolts)	Output Eo (millivolts)	Output less offset, Eo' (millivolts)	P PM	Gain Eo'/Ei
Low range:				
0.00	0.80	0.0	0.20	....
1.00	15.42	5.62	0.75	5.62
2.00	21.40	11.60	1.40	5.80
3.00	27.40	17.60	2.25	5.87
4.00	33.50	23.70	3.00	5.93
5.00	39.70	29.90	3.75	5.98
6.00	46.00	36.20	4.51	6.03
6.65	50.00	40.20	5.00	6.06
High range:				
0.00	0.75	0.00	0.50	....
2.00	15.24	5.40	1.40	2.75
4.00	21.00	11.25	2.00	2.81
6.00	26.80	17.05	4.40	2.84
8.30	32.80	23.05	5.80	2.88
10.00	38.90	29.15	7.30	2.92
12.00	45.00	35.25	8.75	2.94
13.00	48.00	38.25	9.50	2.94
13.65	50.00	40.25	10.00	2.95

[a]Data taken at room temperature.

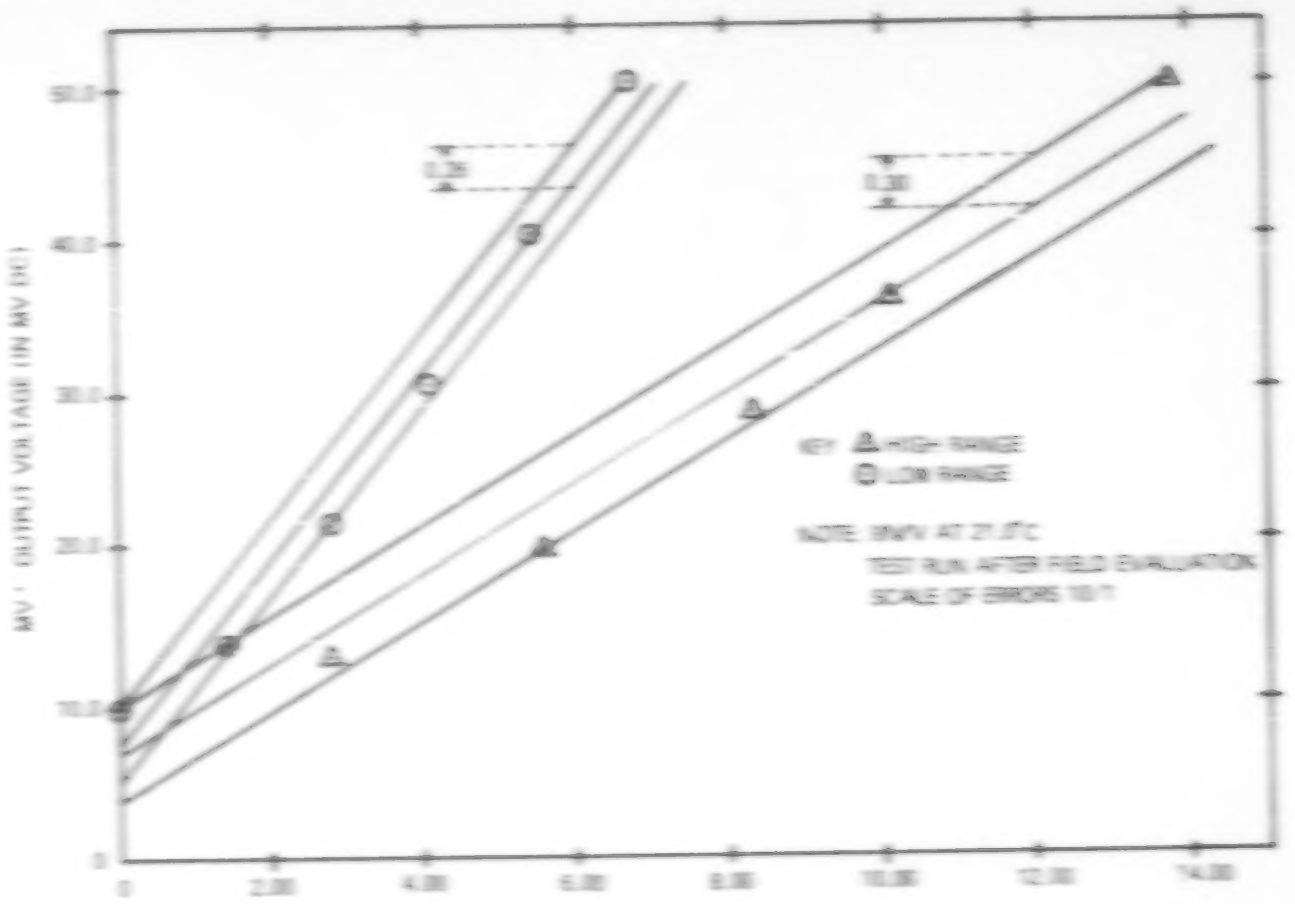


FIGURE 28. INDEPENDENT LINEARITY OF THE [illegible] V.

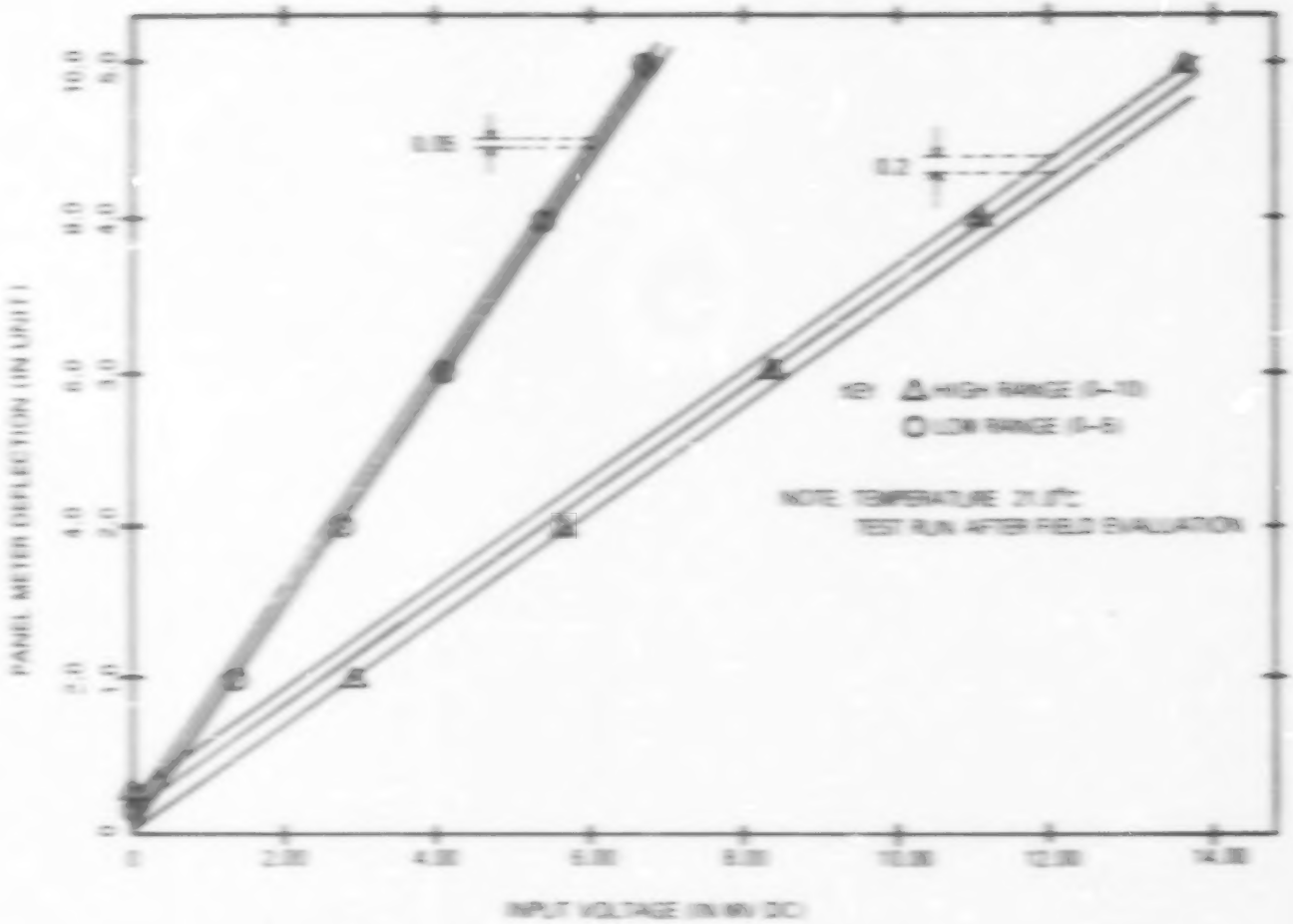


FIGURE 40. INDEPENDENT LINEARITY OF PANEL METER

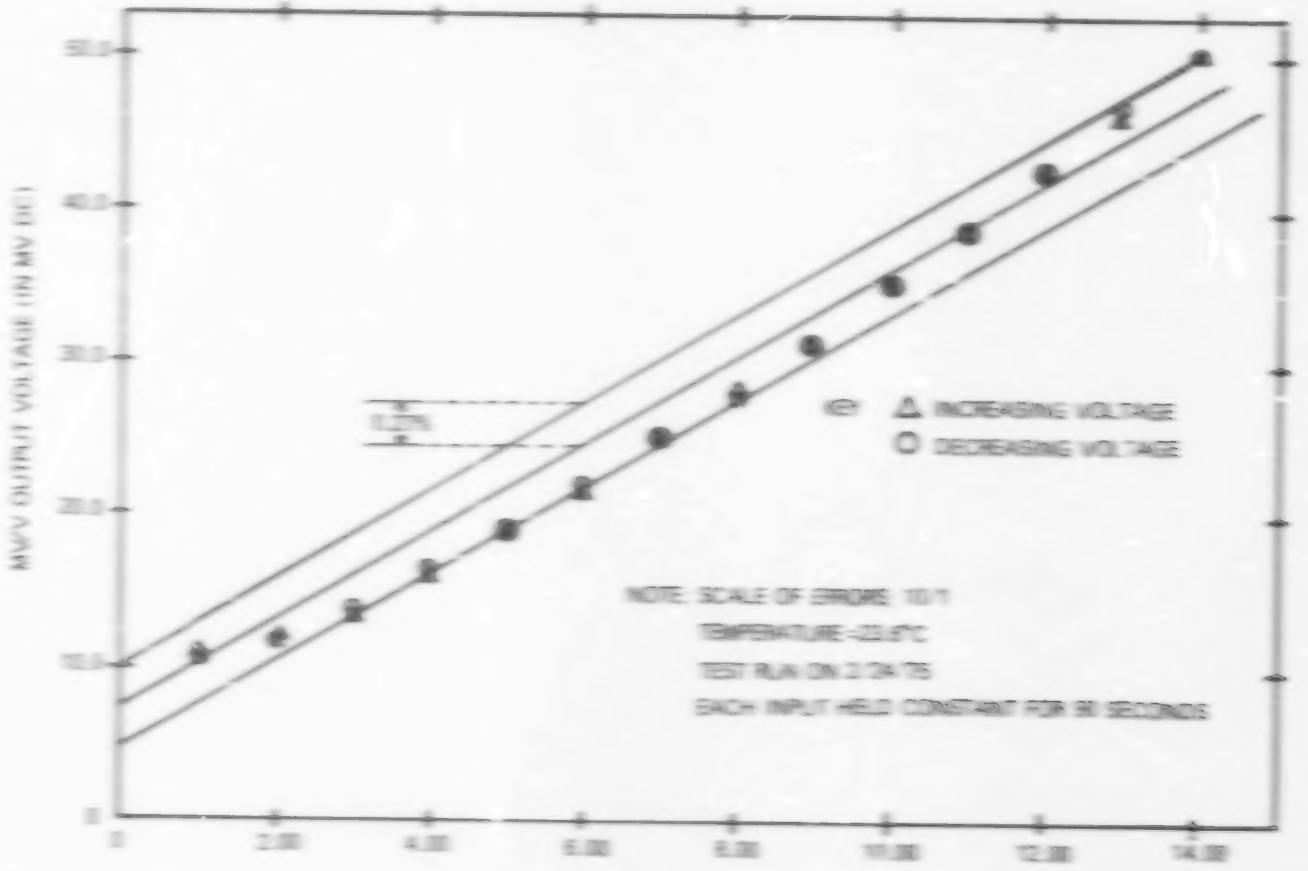


FIGURE 41. INDEPENDENT LINEARITY OF THE MV-V.

The data in Table 12 indicate that the low-range gain increased from 5.62 to 6.06 (or approximately 7.5 percent for the worst case) and that the high-range gain increased a nominal 7.2 percent. The similarity of the gain values displayed in Figures 39-41 and those presented in Table 12 suggests that the long-term (30-day) stability of the MV/V was satisfactory.

The total MV/V linearity data suggest that a nonlinear effect of a nominal ±0.5 percent existed at a given temperature. Exact correlation between ranges was neither intended nor investigated. Although the MV/V had a tendency to shift with temperature before the runaway occurred, the fact that the MV/V was exposed to 200F (93.3C) raises questions as to its exact nonlinear characteristics. It should be recalled that the system was intended to operate over a 0-5 range of 0-5 and 0-10 mg/l but that this was changed in the field at EPA's request to 0-12 and 0-24 mg/l. This modification may have affected the design and also the overall tolerances listed in Table 10.

The final independent linearity data taken indicates that the MV/V's nonlinearity is approximately ±0.27 percent (=±0.5 percent). The data also indicate that hysterisis was negligible because the input was varied from zero to full scale and back to zero. As in the case of Figure 39, the deviation in Figure 40 was multiplied by a factor of 10.

Response

The MV/V is provided with an input RC filter to dampen sudden changes in signal. Transient (time) response data (and the effect of the filter) when the MV/V was exposed to an input signal that produced a nominal 200 percent increase in output signal are displayed in Figure 41. Initial conditions consisted of shorted input terminals, and final conditions responded to an output of about 48 percent, including offset.

Full response was attained within 1.5 seconds for the signal increase, and full response of a nominal 1.2 seconds was attained when the input was short-circuited. Honeywell's specifications call for a response to 90 percent of full-scale step change within 2.5 seconds.

The filter action at 60 Hz was of particular interest since Honeywell indicated that:

1. The filter was "notched" at 60 Hz (i.e., actually attenuated).
2. The primary noise originated from power sources (60 Hz).

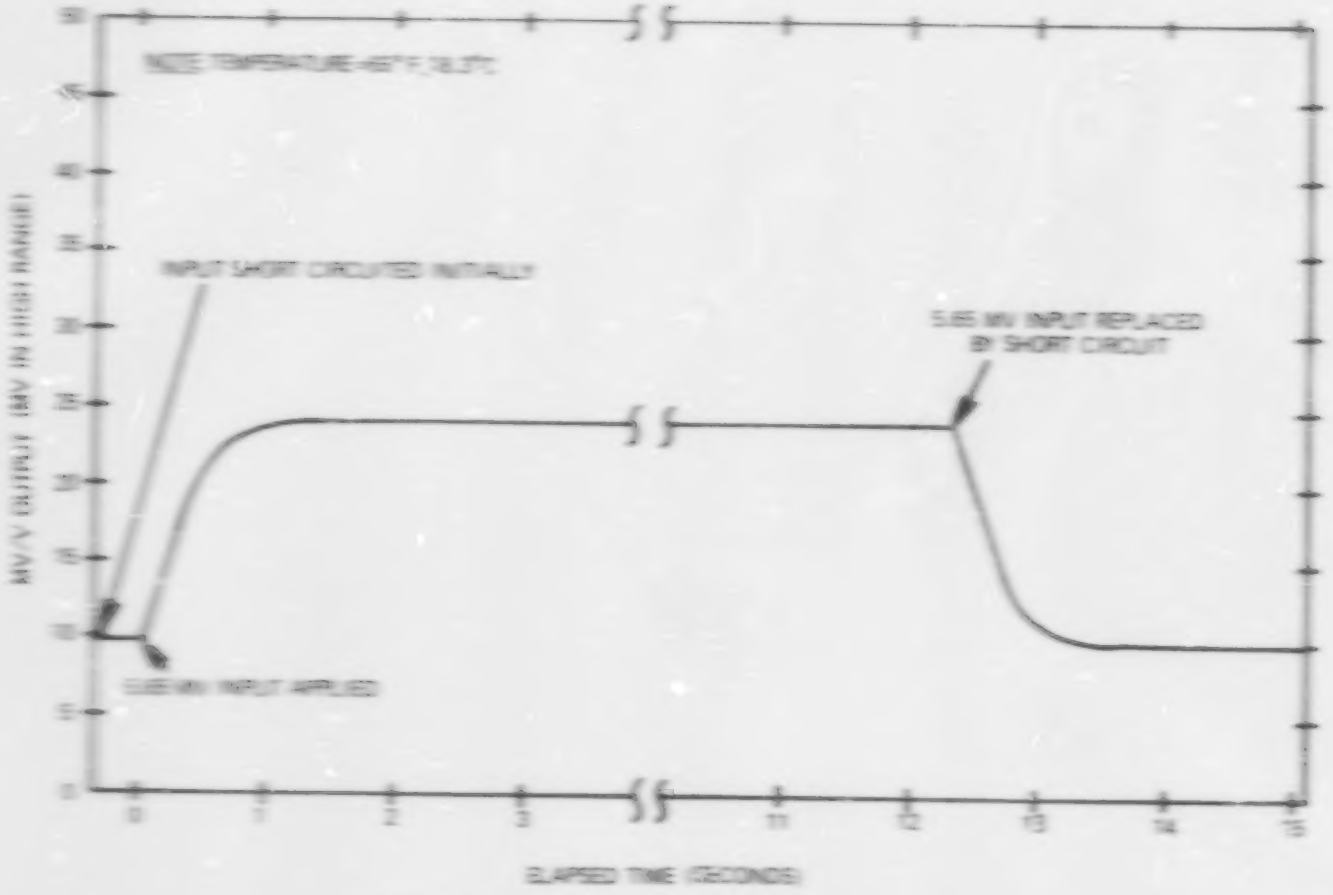


FIGURE 42. STEP-CHANGE RESPONSE OF [illegible] V.

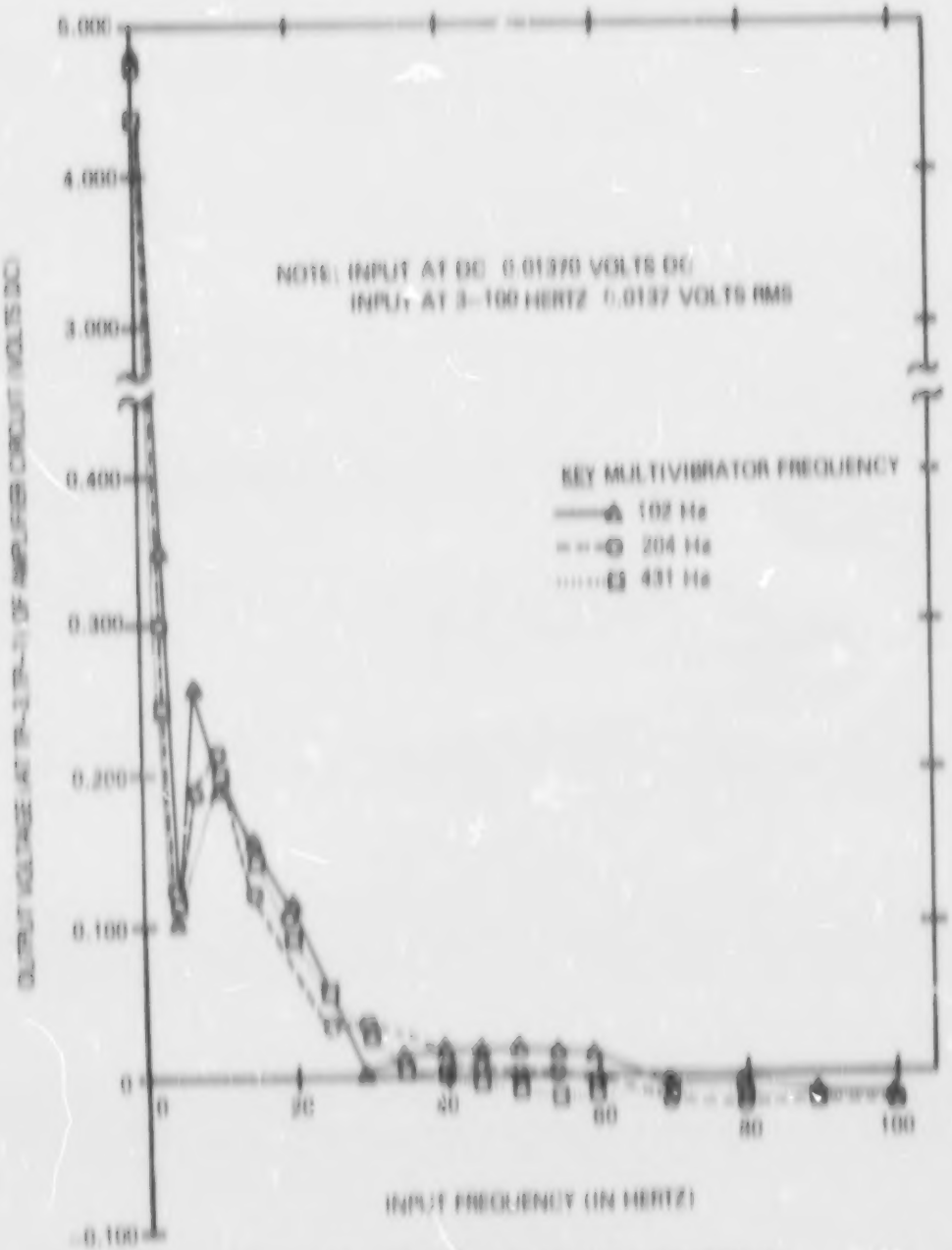


FIGURE 43. FREQUENCY RESPONSE OF THE MV/V.

The frequency response was obtained for the three multivibrator frequencies shown in Figure 43. (The data in Figure 43 were obtained after the chamber temperature runaway and the MV/V was maintained at room temperature.) Three frequencies were chosen to determine if multivibrator drift would affect AC noise attentuation. (No other performance characteristics of the multivibrator frequency were investigated.) The RMS value of the input AC signal was held constant at 13.7 mv, the same magnitude as that of the initial DC potential.

Although each multivibrator frequency produced a slightly different output, the change was so slight that 60 Hz-induced noise is apparently unrelated to the frequencies selected.

The apparent resonance that seemed to occur between 7 and 10 Hz had no effect on overall performance.

SECTION VI

FIELD INVESTIGATION

INTRODUCTION

Field investigation of the Honeywell DO parametric system was conducted at the Hamilton Sewage Treatment facility located on the Great Miami River south of Hamilton, Ohio.

The plant is designed to service a population of 75,000 and can treat 12 million gallons of sewage daily. Design data are summarized in Table 13, and a flow diagram of the plant is displayed in Figure 44.

The sensor was tested in the final settling basin, aeration tank, and effluent chamber.

The final settling basin was chosen to determine how the unit performed in a climate in which the sample velocity across the sensor membrane was minimal. Since the sensor was provided with neither a self-contained sample agitator nor a self-cleaning device, such as a mechanical wiper, it was expected that the output would degenerate with time, as indicated by equation A-1 in Appendix A.

Performance in the aeration tank was of primary concern since Honeywell had designed the system primarily for this application. It was expected that sample flow and turbulence created by aeration would produce adequate sample velocity over the membrane and that a daily cleaning of the membrane would prevent signal degeneration.

The effluent chamber provided two characteristics favorable to making continuous DO concentration measurements: (1) the velocity of the effluent was high (>>1.8 ft/sec[54.9 cm/sec]); (2) the chlorine used would inhibit slime growth on the membrane.

Circles shown in the flow diagram of the treatment plant displayed by Figure 44 indicate location of the sensor during the field tests.

Although reference is made to instrumental differentials, the reader is reminded that investigation at Hamilton Treatment Plant was not a comparison study of several DO parametric systems, but an investigation of one Honeywell design concept. It should also be recalled that the YSI was calibrated each time it was used, and agitated, to obtain a maximum reading. It should further be recalled that the Delta Scientific provided with an agitator had been installed by

Table 13. PLANT DESIGN DATA*

Item	Characteristics
1	Description: Split Activated Sludge Treatment Plant with separate sludge digestion, sludge filtering and chlorination of effluent.
2	Design Average Flow: 12 MGD (million gallons per day)
3	Design Maximum Flow: 18 MGD
4	Design Sewage and Waste Characteristics: Suspended Solids - 350 PPM (parts per million) 5-Day B.O.D. (Biochemical Oxygen Demand)
5	Expected Overall Removal of Suspended Solids at Design Flow of 12 MGD: 75%
6	Expected Overall Removal of 5-Day B.O.D. at Design Flow of 12 MGD: 65%
7	Design Population (1970): 73,000
8	Two Raw Sewage pumps: Rated: 12 MGD Capacity of each pump: Maximum: 20 MGD
9	Two Sewage Pump Engines: Horsepower of each engine: 175 brake horsepower (at 760 R.P.M.)
10	Two Air Blowers Capacity of each blower: 7000 cu. ft. per minute
11	Two Air Blower Engines Horsepower of each engine: 300 brake horsepower (at 690 R.P.M.
12	Detention Period in Grit Chambers at 12 MGD Flow: 10 minutes
13	Detention Period in Primary Tanks at 12 MGD Flow: 2 hours
14	Detention Period in Aeration Tanks Based on Settled Sewage Flow of 6 MGD and 30% Return Sludge: 4 hours
15	Detention Period in Final Settling Tanks based on Average Flow of 6 MGD: 2.8 hours
16	Detention Period in Chlorine Contact Chamber at Maximum Flow of 18 MGD: 15 minutes
17	Total Digester Volume: 480,000 cubic feet
18	Digester Volume per Capita Based on Design Population: 6.5 cubic feet
19	Two Digested Sludge Filters Capacity of each filter: 1250 lbs. digested sludge (dry solids basis) per hour
20	Capacity of Gas Storage Sphere at 40 P.S.I.: 130,000 cubic feet

*Taken directly from Hamilton's Sewage Treatment Plant Brochure.

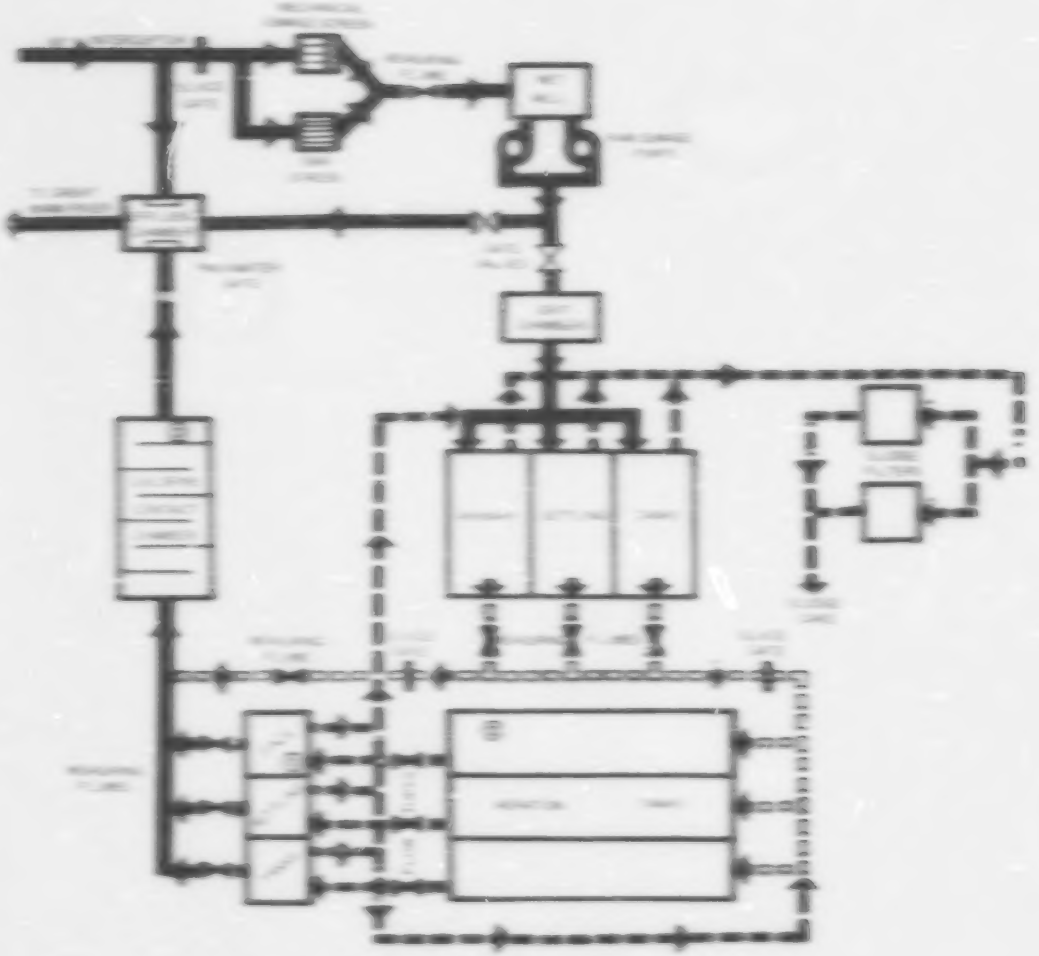


FIGURE 44. SEWAGE FLOW DIAGRAM

Hamilton Sewage Treatment Plant as a primary DO indicator so that deviations between the two instruments (Delta Scientific and Honeywell) are not intended to infer that one or the other is reference data. In spite of difficulty in sampling, the Winkler is reference for the field work. Nonetheless, these peripheral measurements are included for informational purposes to those requiring this type of data.

FINAL SETTLING BASIN (SECONDARY)

Figure 45 displays the sensor installed in the settling basin, and the data accumulated during the test are summarized in Table 14.

The "before turbulence" data were accumulated as follows: the Honeywell MV/V output--including both the panel meter and the strip chart recorder was recorded; the YSI sensor was calibrated and inserted adjacent to the Honeywell, stirred, and its output recorded; and, simultaneously, a sample was drawn for the Winkler determination of the DO concentration.

The "after turbulence" data acquisition was similar: within 5 minutes, the above process was repeated, but the Honeywell sensor was manually agitated by raising and lowering it. The maximum deflection noted was then compared with the second Winkler determination.

The differentials between the Honeywell and Winkler measurements were significantly reduced "after turbulence," but the Honeywell deflections were not consistently within tolerance. This may have occurred because: (1) the sample taken for chemical analysis was not the same as the sample measured by the sensor; (2) chemical components in the sample caused the Winkler to indicate a higher DO concentration level; (3) insufficient sample velocity across the membrane increased the diffusion layer into the sample and reduced the equivalent oxygen current; (4) slime growth on the sensor reduced the signal level.

A device designed and built by plant personnel containing a BOD bottle was inserted in the basin adjacent to the sensor so that the sample for chemical analysis was taken within 2 inches (5 cm) of the sensor. Similarly, the YSI was inserted adjacent to the Honeywell sensor so that we assume an equivalent sample for all measurements. No tests were run to determine whether interference affected the Winkler process. Plant personnel indicated that interference (to the Winkler process) would more likely occur in the activated sludge where the suspended solids were highly agitated and, hence, would become a significant part of the sample for chemical analysis.

FIGURE 46. SENSOR INSTALLED IN SECONDARY SETTLING BASIN

Table 11. MEASUREMENTS MADE IN FINAL SETTLING BASIN

Date & time	Before turbulence				After turbulence			
	Winkler	YSI[1,2]	Honeywell PM	e_1	Winkler	YSI	Honeywell PM	e_2
8/21								
1:00 p.m.	4.0	3.7	1.9	-2.1	3.9	4.0	3.8	-0.1
2:00 p.m.	4.1	4.0	2.4	-1.7	4.0	4.0	3.6	-0.4
3:00 p.m.	4.2	4.0	2.6	-1.6	4.1	4.0	3.6	-0.5
8/22								
9:50 a.m.	1.4	NA	0.3	-1.1	1.5	NA	1.0	-0.5
Sensor cleaned after the "Before turbulence" 10:00 a.m. reading								
10:00 a.m.	1.6	1.6	0.8	-0.8	1.6	1.2	1.2	-0.4
11:00 a.m.	1.8	1.7	0.6	-1.2	1.7	1.8	1.6	-0.1
12:00 N	2.5	2.5	0.9	-1.6	2.5	2.4	2.2	-0.3
1:00 p.m.	3.0	3.2	1.9	-1.1	2.8	2.9	2.6	-0.2
2:00 p.m.	3.5	3.6	1.7	-1.8	3.6	3.6	3.2	-0.4
3:00 p.m.	3.5	3.6	2.3	-1.2	3.6	3.5	3.6	0.0
8/23								
9:00 a.m.	1.6	NA	0.6	-1.0	1.7	1.8	1.6	-0.1
Sensor cleaned after the "Before turbulence" 9:50 a.m. reading								
9:50 a.m.	1.7	1.8	1.2	-0.5	1.8	1.6	1.6	-0.2
10:00 a.m.	1.9	1.8	1.1	-0.8	1.9	1.6	1.6	-0.3
11:00 a.m.	2.1	1.7	1.0	-1.1	2.2	1.7	1.6	-0.4
12:00 N	2.0	2.0	1.6	-1.4	2.7	2.6	2.7	0.0

1. Yellow Springs Instrument®
2. The precalibrated YSI was always agitated to obtain maximum output.
e_1,e_2 = Difference between the Winkler and Honeywell panel meter (H-W).

Minimal sample flow (factor(s) above) across the membrane appeared to be the primary cause of differences - presuming Winkler determinations as reference data. The YSI - following maintenance and calibration - was always agitated and therefore produced data more nearly equal to the Winkler for the "before turbulence" case.

The turbulence data suggest that the sensor was inadequately agitated, but no direct conclusion can be drawn from the cleaning. It is apparent for this type of application that sensors must be provided with: (1) a submerged pump to push water over the membrane surface at a high velocity; or (2) an automatic cleaning device that eliminates the need for daily manual membrane cleaning; (3) both. Delta Scientific and Weston and Stack integrated these functions so that cleaning action is obtained by the sample agitator.

PERFORMANCE IN THE AERATION BASIN

Figure 46 shows the Honeywell sensor installed in the aeration basin, and the data obtained are summarized in Table 15. (Immediately before testing started, the sensor was cleaned, and the parametric system was recalibrated at room conditions, employing sodium bisulphite for zero and saturated tap water for span.)

The DO concentration was periodically determined by the Winkler process, logged from the panel meter of a Delta Scientific instrument in continuous operation, and periodically logged from the YSI panel meter. The deflections of the Honeywell panel meter were logged, and the output from standard test points TP-1 and TP-2 was continuously recorded on an Esterline Angus Speed Servo recorder. The Honeywell sensor was installed within 1 foot (30.5 cm) of the Delta Scientific sensor in the aeration basin and readings were taken with the portable YSI within immediate vicinity of the two sensors. Plant personnel logged data during the second and third work shifts so that data were obtained on a 24-hour basis. During these periods Hamilton Sewage Treatment Plant logged the Delta Scientific and Honeywell outputs.

To reduce the effect that suspended solids might have on the chemical determination, 2 ml of 10 percent copper sulfate (10 grams/100 ml H_2O) were added as soon as the sample was brought to the cement walkway. Chemicals for the Winkler determination were then added, with the sulphuric acid being added after settling had occurred. The sample was taken within 2 inches (5 cm) of the Honeywell sensor.

Since three different DO parametric systems were employed, one would not expect each to indicate identical values in an activated sludge environment due to flowing sample, variations in turbulence, inability

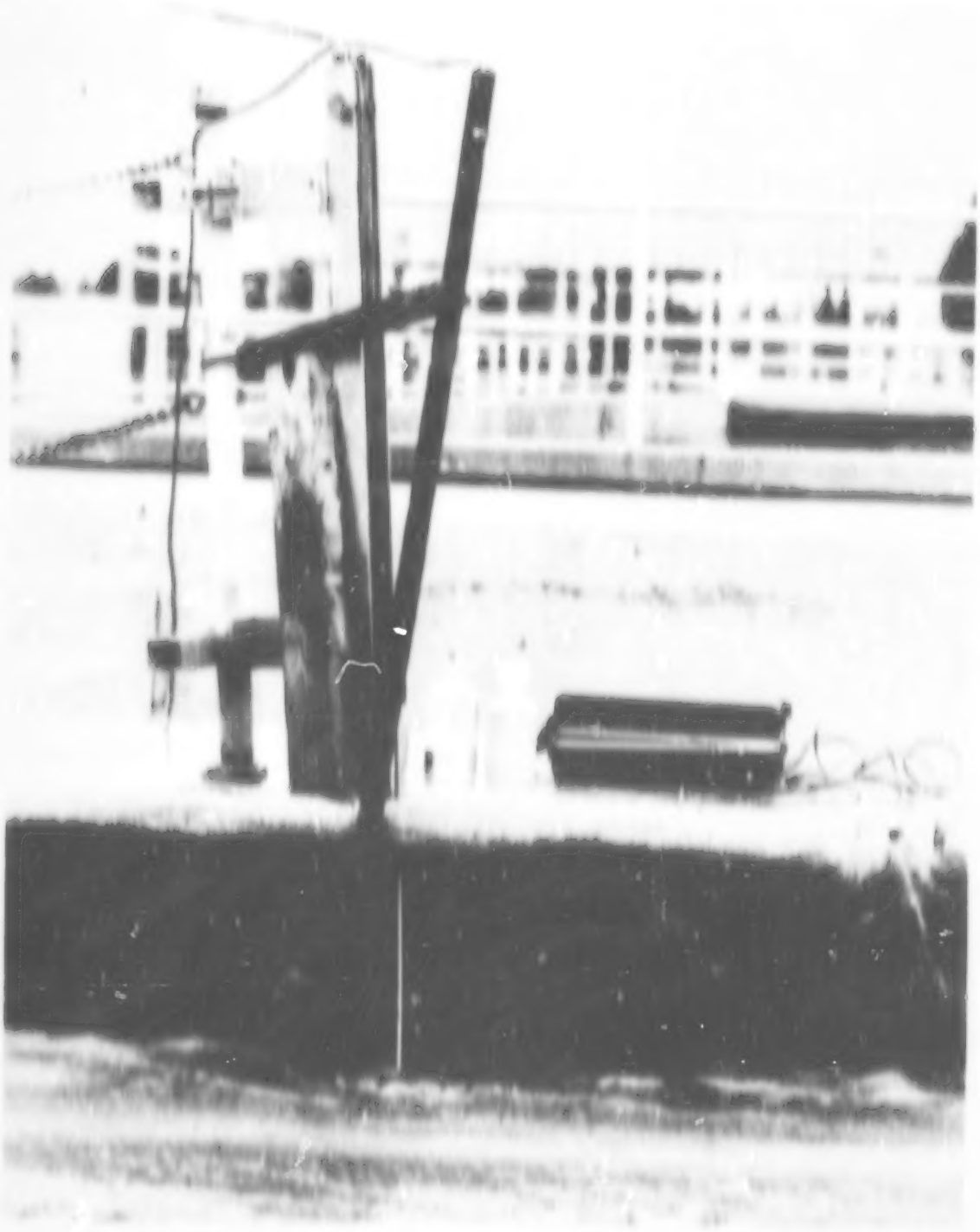


FIGURE 46. SENSOR INSTALLED IN ACTIVATED SLUDGE BASIN.

to measure identical samples, inconsistency in the air bubbles from the aeration system, and tolerances within each design. Occasionally the indicated DO varied during meter reading so that "reader" error would also be expected.

Except for three data points, all Honeywell measurements were within ±0.3 mg/l of the DO concentration determined by the Winkler process. The Honeywell reading exceeded the Winkler determination by 0.6 mg/l on two occasions, and was low by 0.4 mg/l in one case.

Seventy-nine percent of the differentials between the YSI and Honeywell were within ±0.3 mg/l. Four data points indicated a difference of ±0.5 mg/l between the two instruments.

Seventy-seven percent of the differences between the Delta Scientific and Honeywell instruments were within ±0.3 mg/l and 23 percent of the differentials were within ±0.6 mg/l excepting one that was 1.8 mg/l. The latter was discounted.

For all data accumulated, including 56 data points during the preceding week, the differentials between the Honeywell and Delta Scientific were within ±0.4 mg/l 90 percent of the time.

Employing the Winkler as reference, the mean and standard deviations for the Honeywell system were 0.118 and 0.256, respectively.

Several problems occurred in obtaining the data shown in Table 15. The inking system on the recorder failed several times, and factory replacements had to be installed. Frequently, samples taken for the Winkler process were too turbid, and the titration was invalidated. The addition, however, of copper sulfate reduced this interference. On frequent occasions, a series of spikes was recorded following sensor cleaning; a typical series is displayed in Figure 47. This was corrected by dipping the tip of the sensor into a sulphuric acid solution (pH = 2.5) and not mechanically wiping the sensor.

EFFLUENT CHAMBER (CHLORINATED)

Before the sensor was installed in the effluent chamber, its cap was removed and sludge (oxides of silver) was removed from the cathode. The parametric system was then recalibrated employing sodium bisulphite for zero and saturated tap water for span. The sensor was installed and moved to an approximate 45 degree angle by the force of the water, which had a minimum velocity of 15 feet per second (4.8 m/sec) at the sensor (Figure 48). The sensor was not cleaned during the test. Samples were drawn periodically for the Winkler determination, and peripheral measurements by the YSI were recorded. The YSI

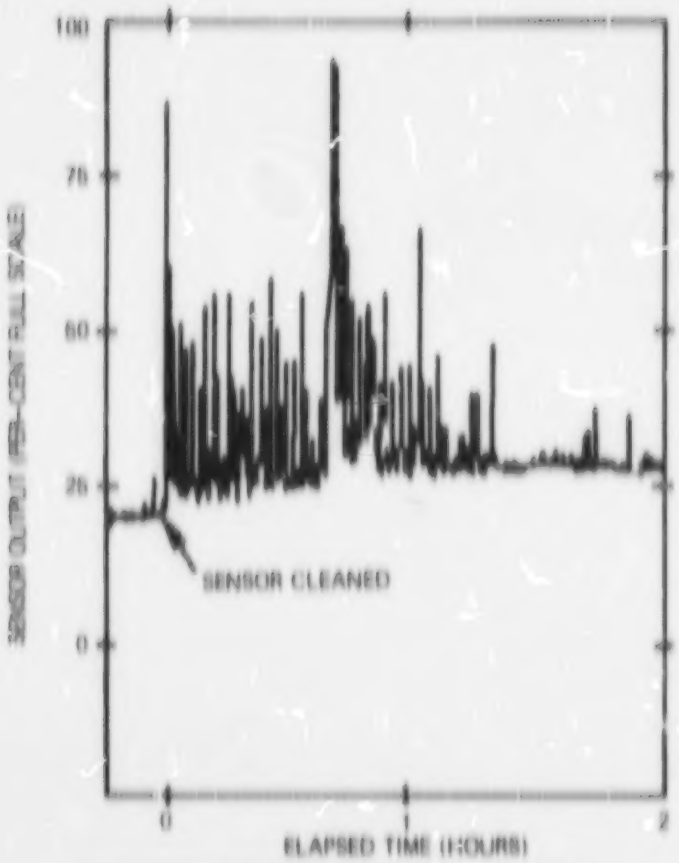


FIGURE 47. SENSOR OUTPUT IN ACTIVATED SLUDGE FOLLOWING MANUAL CLEANING.

FIGURE 48. SENSOR INSTALLED IN CHLORINATED EFFLUENT.

was calibrated on a daily basis employing the manufacturer's procedure as outlined in the YSI manual (Model 51A). Similar to the previous tests, the YSI was inserted adjacent to the Honeywell, and samples for the Winkler were extracted from a position within 2 inches (5 cm) of the Honeywell sensor. Data for the test are summarized in Table 16.

Although data were accumulated continuously on the recorder, only data recorded from the Honeywell panel meter are tabulated. Midway during the test, the recorder developed a 2.5 percent down-scale offset; the fault was corrected, disrupting the continuity in data.

The ability of the Honeywell sensor to operate unattended, continuously, and successfully (well within ±0.3 mg/l) for 1 week was traceable to two basic facts: the chlorinated condition of the effluent and its high discharge velocity (greater than 15 feet per second [4.8 m/sec] at the sensor).

Table 16. MEASUREMENTS MADE IN CHLORINATED EFFLUENT

Date & time	Winkler	YSI	PM	ϵ_1	ϵ_2	ϵ_3
9/4/74						
4:30 p.m.	2.0	---	2.2	+0.2	---	---
9/5/74						
10:00 a.m.	4.5	---	4.4	-0.1	---	---
11:00 a.m.	4.0	4.3	3.9	-0.1	-0.4	+0.3
12:00 N	4.1	4.1	4.0	-0.1	-0.1	0.0
1:00 p.m.	3.6	3.8	3.8	+0.2	0.0	+0.2
2:00 p.m.	3.6	3.8	3.6	0.0	-0.2	+0.2
3:00 p.m.	3.5	3.6	3.6	0.0	-0.1	+0.1
9/6/74						
9:30 a.m.	3.5	---	3.4	-0.1	---	---
10:30 a.m.	3.4	---	3.4	0.0	---	---
11:00 a.m.	3.2	3.2	2.9	-0.3	-0.3	0.0
12:00 N	2.4	2.5	2.4	0.0	-0.1	+0.1
1:00 p.m.	2.5	2.5	2.4	-0.1	-0.1	0.0
2:00 p.m.	2.6	2.6	2.5	-0.1	-0.1	0.0
3:00 p.m.	2.6	2.6	2.5	-0.1	-0.1	0.0
9/8/74						
12:30 p.m.	3.6	3.7	3.7	+0.1	0.0	+0.1
9/9/74						
12:00 N	2.8	2.9	2.8	0.0	-0.1	+0.1
1:00 p.m.	2.8	2.8	2.9	+0.1	+0.1	0.0
2:00 p.m.	2.8	2.9	2.8	0.0	-0.1	+0.1
3:00 p.m.	2.8	2.8	2.8	0.0	0.0	0.0
9/10/74						
3:00 p.m.	2.8	---	2.8	0.0	0.0	---
		Mean = $\bar{x}$		-0.0200	-0.100	0.0800
		Standard deviation = s(x)		0.115	0.121	0.0941

Key:
YSI = Yellow Spring Instrument DO system
PM = Panel Meter of Honeywell Instrument DO system
ϵ_1 = PM - Winkler
ϵ_2 = PM - YSI
ϵ_3 = YSI - Winkler

The Delta Scientific Corporation[9] dissolved oxygen sensor was not transferred to the effluent raceway for this test.

SECTION VII

EVALUATION OF MANUALS

Honeywell provided two manuals on the DO parametric system: (1) #830-10 operator's manual for the sensor assembly, and (2) #542012-11-121-200001-12 operator's manual for the MV/V. Each manual is of a modular design and contains the following basic sections: description, installation, operation, maintenance, theory, service, parts list.

The MV/V manual contains many more sections than the sensor assembly manual, because the MV/V is electronically more sophisticated and contains many devices, as noted earlier.

As a guide to this Section (VII), Section 5.00 of reference 5 was employed.

The following line items are intended for the beginner as it points out several areas that the Honeywell manuals either exceed EPA's current requirements, are not applicable, or emphasizes an area that the authors believe are necessary for this type of instrumentation.

Section 5.00	Not applicable for this particular project. However, Honeywell has been known to provide as many copies of each manual as the customer requires.
Section 5.04	Meets - This section is instructional (both manuals).
Section 5.07	Meets - This section is instructional (both manuals).
Section 5.08	Sensor Manual - The Honeywell manual indicates that the sensor "is not calibrated separately but as a parametric system with its matching conditioner." Due to the basic design philosophy, it was possible and convenient to investigate each separately for given tests.
Section 5.10	Honeywell provides many additional engineering drawings and some exploded diagrams that clarify any photographic vagueness.
Section 5.12	All parts are available from Honeywell.

Section 5.14 Cost not included.[1]

Section 5.15 Cost not included.[1]

Section 5.16 Cost not included.[1]

OVERALL APPRAISAL OF MANUALS

Overall, the Honeywell manuals provide more than adequate information to permit successful use of the product and they are also tutorial.

Because Honeywell manufactures a variety of products that employ similar components, the modular sections can be inserted in other manuals. This affects the numbering of figures and causes a certain amount of inconsistency.

SENSOR MANUAL

There are several typographical errors regarding the chemicals needed: Section 131-33, Page 3 Physical data; 535-3, Page 2; 636-9, Page 3; 639-9, Page 6.

The summary of material specifications, Section 131-33, Page 3, might be more easily understood if the type of material followed the function: Cell Body - Unplasticized PVC, etc., i.e., a horizontal rather than a vertical format.

The page numbering required because of the modular arrangement is not as straightforward as other manuals that are used for similar designs. It would be better to number pages consecutively, although there is merit in giving each section its own numbering system. Perhaps each manual could be provided with a unique table of contents. This could be accomplished via the Honeywell Data Processing function and merely key-in the functional descriptions required. The printout would provide the table of contents and the computer could print the entire manual.

MV/V TRANSMITTER MANUAL

The MV/V transmitter manual reveals excessive design strategy and a generalized product suitable for many applications.

1. Costs have been omitted because of variations in economics. GSA schedule prices are available to Federal Agencies and open-market prices are available from the Honeywell Offices.

The manual is also modular in format, and this has caused several details to be omitted. Of particular concern is the numerical subscript for the components, i.e., there are several IP-1's, Q1's, R1's, etc., since the numbering is unique to each circuit card. A double subscript or alpha-numeric subscript system might be more direct.

Additionally, a clearer interconnection drawing between cards would be desirable - for example, the feedback through the measuring circuit is not obvious.

Modularity and variety of options make schematic interpretation difficult.

Page numbering comments are similar to those for the sensor manual.

Honeywell personnel have been exceptionally liberal in providing design information so that anyone desiring to work successfully with this product should have no problems.

SECTION VIII

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9. Delta Scientific Corporation, Linderhurst, New York 11757.

APPENDIX A

BACKGROUND ON DISSOLVED OXYGEN MEASUREMENTS

DO is theoretically present in all open bodies of water, but waters void of DO are generally heavily polluted, so that DO is one of the more frequently measured parameters. With some exceptions (such as an anaerobic operation) DO is a basic ingredient to the sustaining of aquatic life and is one of the primary measurements made in sewage treatment plants.

In an aerobic domestic (organic) sewage treatment plant, i.e., one in which the waste, air (or "pure" oxygen), and microorganisms are mixed, oxygen is one of the variables which determines how effectively a treatment function operates. If saturation is reached, additional oxygen bubbles through the mix to the atmosphere. Under some conditions additional aeration could be uneconomical so that measurement of DO within the aeration tank can be used to control the aerators saving oxygen, energy, machinery wear, and cost.

Overall, D. G. Ballinger's* considerations for employing unattended instruments (quiescent monitoring) in water pollution control programs can also be used in process control.[A-1] In his paper he states that "the first factors to be considered are the specific objectives of the control (legal) programs."

"Among the objectives may be:

1. To collect information on sources of pollution and the impact on water quality, in support of regulatory activities. [Treatment effluents are being regulated.]†

2. To obtain real-time data for the protection of public water supplies. ["Raw material" sources for water supplies are generally rivers and lakes into which industrial effluents have been discharged.]

3. To obtain sufficient data to develop mathematical models for water quality management. [Sewage treatment facilities can be fully automated and computer controlled once favorable models are developed.]

*Director, Environmental Monitoring and Support Laboratory - Cincinnati, Office of Research and Development, U.S. Environmental Protection Agency.
†Remarks in brackets are those of the authors.

4. To record long-term trends in the quality of resources." [This could easily include long-term trends related to sewage plant influents and effluents.][*]

DO has been measured in rivers, streams, lakes, and oceans for a number of years to identify many problem areas. One of the major pollution sources causing excessive BOD and reduced DO levels is overburdened domestic sewage treatment plants.

Oxygen is dissolved in streams, lakes, and oceans in accordance with Henry's Law[†]. The solubility of oxygen is a function of the water's temperature, pressure, and salt content.[A-2] As the temperature increases, the solubility of oxygen decreases, and as the salt content increases, a "salting out" phenomenon also reduces the solubility.

METHODS USED TO MAKE DO DETERMINATIONS

There are several methods for determining DO in water samples:

1. Winkler process
2. Application of paramagnetic properties of DO
3. Galvanic cell, exposed electrodes
4. Galvanic cell, membrane covered assembly
5. Passive cell, membrane covered assembly.

1. The Winkler process employs wet chemical techniques that culminate in the titration of free iodine. Although fully documented in Reference A-2, it is well to consider the following:

   a) Several chemical modifications to the Winkler process are necessary to compensate for ionic interferences unique to the samples.
   b) Generally, low-temperature, nearly saturated samples are titrated almost to the end point (1-2 mg/l) before starch or thyodene is added to obtain a near purple-like color. If they are added too early, colored, undissolved particles remain, which affect the true end point.

[*]Remarks in brackets are those of the authors.
[†]"The mass of a slightly soluble gas that dissolves in a definite mass of a liquid at a given temperature is very nearly directly proportional to the partial pressure of that gas. This holds for gases which do not unite chemically with the solvent." (Handbook of Chemistry and Physics, 43rd Edition).

c) In some applications, such as in sewage aeration basins, it is difficult to obtain a representative sample and to obtain consistent results because of the suspended solids present.[5]

2. The Hays Company developed a DO analyzer based on the paramagnetic properties of oxygen, but the device employs a rather cumbersome magnet. This instrument was investigated by J. Weeks[A-3] and requires no further comment.

3. Hertz[A-4] and Mancy[A-5] have summarized the history and operation of galvanic cells. Based on their investigations and those of others,[A-4,A-5] companies such as Union Carbide[A-6] and American Limnetics[A-7] developed DO sensors that employed thallium cathodes. The Union Carbide sensor assembly used a silver-silver chloride reference electrode but performance was unsatisfactory. In these two designs, the exposed thallium became poisoned by impurities that affected overall response. The Union Carbide sensor response was also affected by particles of thallium that dropped from the base metal, and left voids. The fault was traced to manufacturing procedures.[A-8]

4. Mancy and Westgarth[A-9] and others pioneered the development of membrane-covered galvanic cells. Generally, the galvanic cell employs a platinum cathode, lead anode, either polyethylene or teflon membranes, and either KI or KOH electrolyte.

   Weston and Stack, one of many companies that manufacture a DO parametric system, employs a galvanic cell, teflon membrane, platinum cathode, lead anode, potassium iodide electrolyte, and a self-contained sample agitator.[A-10] In the absence of oxygen, the output of the sensor is virtually zero.[A-11]

5. The passive DO sensor (electrolytic cell) is provided with devices similar to those found in a membrane-covered galvanic cell, but an external reduction potential is applied and, in the presence of oxygen, current is generated.

   Membrane

   Both teflon and irradiated polyethylene membranes have been employed. Honeywell employs 1-mil teflon in the sensor

[5] J. Winkler indicated that the Hamilton, Ohio, plant has been employing instrumental DO parametric systems instead of the Winkler process for these reasons.

investigated. Although somewhat overly simplified, the "paths" ("canals") through which oxygen diffuses in the membrane to the cathode seem to be randomly located in teflon membranes but more systematically located in irradiated polyethylene. A sketch of this simplified concept is illustrated by Figure A-1, without proof,[A-12] and each section is symbolic of a unique membrane.

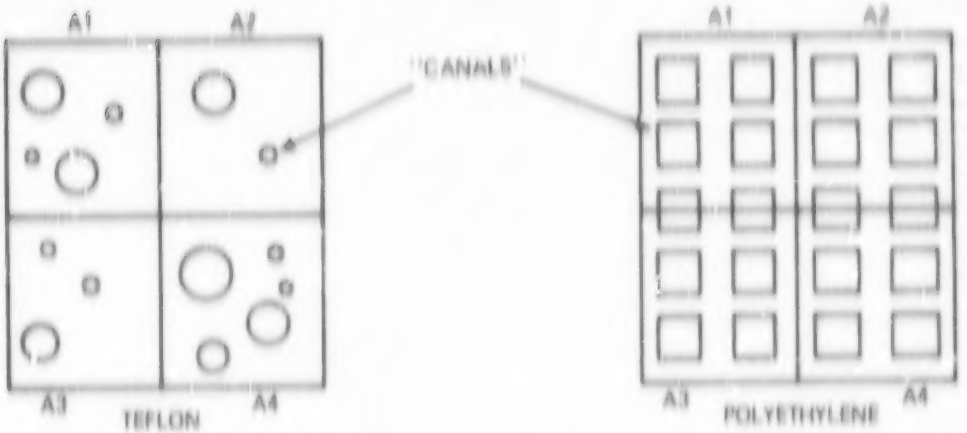

FIGURE A-1. SIMPLIFIED CONCEPT OF MEMBRANE "CANALS".

It is evident that section A1 of the teflon membrane has a different sensitivity than does section A4. Since the polyethylene membrane exhibits more consistency among sections, it is more consistently sensitive to the diffusion of molecular oxygen.

Although considered to be more favorable than polyethylene from a maintenance viewpoint, teflon appears to have "plastic memory" because temperature cycling affects "sensitivity" (see Laboratory Investigation Section). Polyethylene membranes lost their sensitivity within several hours when used to measure DO under supersaturated (20 mg/l) conditions in the Little Miami River. The loss was traced to the growth of rotifers, stalk protozoa, diatoms, and fibers* on the membrane.

*Identified by Dr. C. Weber, Chief, Aquatic Biology Section, EMSL-Cincinnati, Ohio.

Sample Velocity at Membrane

Oxygen that has diffused through the membrane and is reduced at the cathode must be replenished at the sample-membrane interface to maintain measurement integrity. This is effected by providing sample velocities greater than 1.0 foot per second (30.5 cm/sec) across the membrane. The effect of sample velocity on diffusion current is approximated by

$$i(v) = K(1-A_{v}^{-Bv}) \qquad (A\text{-}1)$$

where i(v) = current produced by reduced oxygen, amperes

K; A; B = constants of proportionality

v = velocity of sample, cm/sec

Most manufacturers consider 1.8 feet per second (55 cm/sec) adequate velocity but the Dutch company, Philips, employs 6.6 feet per second (2 m/sec) velocity over the sensor area which also aids in scrubbing the sensors.

Some manufacturers provide vertical flow patterns (this is also recommended by Honeywell)* perpendicular to the membrane surface, but in some cases the vertical impingement on the sample has caused mud and sand particles to adhere to or penetrate the membrane, which damages it and lowers its sensitivity. For one DO parametric system,[A-13] the authors designed a nozzle which provided an almost horizontal flow over the membrane, and the main stream line was directed at the center of the sensor membrane starting 10° below the horizontal. Flow cells designed by the Schneider Instrument Company followed a similar philosophy employing tangential influent and effluent paths. By mounting the Schneider sensors off center in these cylindrical cells, maximum benefits of "high velocity" at nearly horizontal flow are obtained.[A-14]

Sensor Electrodes

In accordance with EPA's specification,[A-15] the Honeywell employs a gold cathode and silver anode.

*In selected applications.

Platinum cathodes have been used in some other sensors, but experiments suggested that oxides form on the cathode and decreases its sensitivity.

Reasonably high surface-area ratios (anode/cathode) are preferred for long-term stability, but ratios between 25 to 100 have proven adequate for 6 to 12 weeks of operation. Sensor maintenance frequency rises as the ratio decreases. The Honeywell sensor has a ratio of approximately 400 and employs a gold cathode alloyed with small quantities of platinum-silver to improve its machining capability. The button is approximately 1/8 inch (0.318 cm) in thickness to 3/32 inch (0.237 cm) at the center. There is no apparent difference between the performance of this cathode working against its silver anode and the gold-silver electrode assemblies.

In several experiments performed by the authors on designs employing gold cathodes, silver ions plated-out on the gold shoulder exposed to the electrolyte and produced a zero offset current. Extreme care must, therefore, be exercised when the assembly is manufactured.[A-15] In the absence of high quality control, an auxiliary zero offset circuit compensates for "silver ion" current.

The migration of silver ions to the cathode was predominant in one design that employed carbon, because silver crystalized near the cathode-membrane junction. This eventually led to a short-circuited sensor, because the anode and cathode were only 1/2 inch (1.99 cm) apart.[A-15] The manufacturer attempted to "filter" the silver crystals and/or silver ions by adding kaolin to the electrolyte but did not succeed. Using a similar concept, however, Gealt developed a screen that inhibits oxides of silver (sludge) from settling on the cathode, thus preventing reduction in sensitivity, spurious signals, and offset currents.[A-16]

MacInnes describes a silver coulometer which is functionally similar.[A-17] The coulometer consists of a platinum cathode bowl filled with a silver nitrate electrolyte, a silver anode, and a cup of porous ceramic material that surrounds the silver. He states, "During electrolysis, the anode disintegrates to some extent so that particles become detached and drop off. At the same time a dense 'anode slime' is formed, the composition of which is still in doubt. The porous cup protects the cathode by

catching the particles which fall from the anode and it also obstructs the diffusion of the anode slime into the cathode chamber." The effectiveness of the screen (cup) depends on the manufacturing techniques discussed later.

Electrolyte

There are several types of electrolytes, including KCl and KOH. The normality of a given electrolyte affects the transient response.[A-19] Additionally, Maney, et al, also note that carbonates form within the electrolyte because the membranes discussed are permeable to carbon dioxide, which reduces their sensitivity.[A-18]

Honeywell employs a combination of KCl and KOH (2N KCL and 0.5N KOH).

In the absence of KOH, Honeywell says that hydrogen peroxide will probably form and raise the output during sensor break-in.[A-19] Tests indicate that sensors require a 1- to 4-hour break-in; this is normally performed at the company before installation. Under selected conditions, it would seem that the KOH generated (with KCl electrolyte) during break-in would be sufficient to reduce the amount of hydrogen perioxide formed and lower the output increase observed by Honeywell. The authors did not, however, run tests to substantiate this possibility.

Temperature Compensation

The gas-permeable membrane is temperature sensitive so that at a constant pressure and DO concentration, an increase in temperature causes more oxygen[a] to diffuse through the membrane, thereby increasing the sensor output. Thus, in saturated samples, an uncompensated sensor produces more output at 95F (35C) than at 35F (1.7C).

Honeywell locates the total compensating network at the sensor to generate an mv potential that is proportional to the DO concentration (in fresh water). This approach is similar to that reported by Carritt and Kanwisher.[A-20]

Other designers locate the thermal components with the sensor, but schematically show them as being in the signal-conditioning device. Related network components are actually located in the signal conditioner.

[a]Oxygen activity also is affected as noted in the references.

thermal response depends on the total mass of the sensor assembly, including the electrolyte, body, thermistor, and membrane. To achieve a balanced thermal response, Honeywell has mounted the thermistor so that it is exposed to the sample. This arrangement obtains 98 percent of a step change in temperature (and DO) within 2 minutes.

Reduction Potential

In the presence of 800 mv, oxygen that has diffused through the membrane into the sensor assembly is reduced at the negative gold cathode. Experiments have shown that the output for selected sensors remains relatively constant when the reduction potential plateau lies between 650 and 900 mv.

However, in experiments performed in EMSL on 10 DO sensors obtained from the Schneider Instrument Company, the transient response was improved when the reduction potential was reduced from 800 to 650 mv. The authors thought the improvement may have been related to the manufacturing technique used and the fact that the diffusion layer emanated away from the sensor cathode into the immediate electrolytic film. At 800 mv, excessive overshoot occurred when the sensor was transferred from the RT to the CT mode (saturated, 65F [18.3C] to 35F [1.7C]). At 650 mv, the overshoot was reduced, and the response was within tolerance in less than 2 minutes compared to 3-5 minutes when the reduction potential was higher. (In these tests, the temperature compensation and analyser were the same, as were all other conditions, except the sensor.)

With increased reduction potential, other gases can be reduced and the output current increased.[11,21]

In one design, when the anode was internally connected to about 5.0 volts DC during a test, gases formed and the increased internal pressure caused the membrane to balloon,[11,12] but this problem was eliminated by changing EPA's specifications and design parameters.

In the Honeywell design, the sensor assembly generates a potential that can be connected or not connected. Hence, prolonged temperature-stability tests of the analyser employing the "check" will not affect the sensor.

Sensor Body

In cooperation with the Schneider Instrument Company in an experiment employing a teflon body, EMSL personnel found that the response was erratic during transient analysis.[A-12] A smooth response was obtained undr similar conditions when a PVC body was tested. Improved performance with PVC was traced to its lower temperature coefficient (80 μcm/cm/°C). Teflon, which has a temperature coefficient of 147 μcm/cm/°C contracted at lower temperature and this caused the membrane to balloon. This, in turn, increased the electrolytic film between the cathode and membrane and affected the response.

Most companies currently employ PVC as the base material for the DO sensor.

OTHER CONSIDERATIONS

In the beginning of this appendix, single point measurement of dissolved oxygen for possible aerator control application was implied. The Honeywell system lends itself to multipoint (m) measurements and "average point" control philosophy. The sensor assembly produces a temperature compensation potential linear in dissolved oxygen so that several sensor outputs can be summed in an operational amplifier with a gain of 1/m, and then connected to the input of the MV/V. The single output of the MV/V would serve as the "average control" potential.

APPENDIX A

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APPENDIX B

THEORY

Only selected considerations on theory of sensor components behavior are provided below as the literature included theoretical aspects in great detail.[B-1,B-2]

When molecular oxygen diffuses through the membrane and the electrolytic film to the cathode (-800 mv), the following reaction occurs.[B-3]

$$4e + O_2 + 2H_2O \rightarrow 4OH^- \qquad (B\text{-}1)$$

in which e is a negative charge.

When the electrolyte is KCl, the +800 mv silver anode reacts with the chloride ion as follows.[B-4]

$$4Ag + 4Cl \rightarrow 4AgCl + 4e \qquad (B\text{-}2)$$

When the electrolyte is KOH, the silver anode is oxidized:

$$4Ag + 4OH^- \rightarrow 2Ag_2O + 2H_2 + 4e \qquad (B\text{-}3)$$

The current measured can be calibrated in terms of the oxygen content (mg/l) of the sample, dependent upon design as the reduced oxygen is a function of oxygen activity, temperature, and partial pressure. Clancy notes that the total solubility of oxygen at constant pressure is related to oxygen activity:[B-5]

$$P = HA_{O_2} = H\beta C \qquad (B\text{-}4)$$

where P = partial pressure

H = Henry's Law constant

A_{O_2} = activity of molecular oxygen

β = activity coefficient

C = concentration of DO

He further shows that the diffusion current (proportional to reduced oxygen) is given by

$$i_d = \frac{sFAP_M}{b} A_{O_2} \qquad (B\text{-}5)$$

where i_d = diffusion current, amperes

F = Faraday constant

s = the number of electrons transferred

A = cathode area

P_m = membrane permeability

b = membrane thickness

Briggs shows a similar relationship, except that A_{O_2} is replaced with C_s, the partial pressure of oxygen in the sample.[B-6]

Because large anode/cathode surface ratios have been noted,[B-7] an element of qualification is necessary in considering equation B-5. A high ratio obtained with a small cathode diameter tends to produce a lower sensitivity, which requires a change in the analyzer design. Additionally, if an offset current exists, its magnitude could be comparable to that of the signal current and also have an effect on the design. Normally, a cathode having a nominal diameter of 0.20 inches (0.51 cm) and an anode/cathode ratio of 40 or more is suitable for continuous field monitoring.

If it assumed that the electrolytic film between the inside of the membrane wall and the cathode surface is infinitesimal and that instantaneous reduction takes place as the oxygen passes from the membrane, the inside surface of the membrane acts as a sink under steady-state conditions, and the gradient in the permeation equation of Fick's Law becomes a constant.[8]

[8]The reader is referred to Reference B-2 to solve Fick's second law for the transient response.

$$P = -D \frac{\partial C}{\partial x} \qquad (B\text{-}6)$$

where P = permeation

D = diffusion coefficient

$\frac{\partial C}{\partial x}$ = concentration gradient of oxygen through the membrane (axis perpendicular to membrane surface).

Hence, the permeation can be rewritten as

$$P = D \frac{C_1 - C_2}{\ell} \approx \frac{DC_1}{\ell}$$

where C_1 = incoming oxygen concentration and assumed constant

C_2 = outgoing oxygen concentration

ℓ = membrane thickness

Under the assumption presented above, C_2 is zero and P is reduced to the approximation.

This is obviously simplified since some manufacturers provide thin tissue between the membrane and cathode to assure that electrolyte is present at the cathode. In absence of tissue, capillary action provides electrolyte at the cathode.[B-8] The cathode need not be restricted to a line, as implied by equation B-6, but can be curved, so that spherical coordinates may be a closer approximation.

Barrer[B-9] summarizes the principal characteristics of the permeation process regarding the passage of gases through membranes and states:

> "(1) The Fick diffusion Law $P = D \frac{\partial C}{\partial x}$ (P denotes the permeability and D the diffusion constant) is true in the stationary state. [The authors call this 'steady-state.']
>
> (2) Stationary flow is established in a period of minutes, the actual time depending upon the temperatures. [Refer to the transient response data on the Honeywell sensor.]

(5) The permeation rates are usually proportional to the pressure and inversely proportional to the thickness of the membrane [see equation B-5 above].

(4) The velocity of diffusion is only slightly altered by roughening the outgoing surface. [This is not to imply that diffusion occurs through a choked 'canal' in the membrane.]

(5) The passage of an electric discharge through either the glass wall or through the gas (hydrogen or helium) has no effect upon the diffusion rate.

(6) The process of permeation through these (glass) membranes is highly selective and markedly temperature dependent....." [Note discussion on temperature compensation.]

Oxygen profiles in membranes and electrolyte are discussed by Mancy as a time function.[B-9] After the transient response has been completed, Mancy's approximation for steady-state DO concentration through the membranes agrees with that derived from equation B-6.

Briggs and Viney[B-10] show how temperature affects the DO cell output current by the following equation:

$$i(T) = Ke^{-J/T} \qquad (B-7)$$

where $i(T)$ = cell output current

K, J = constants for a particular cell geometry and cell membrane

T = temperature, degrees Kelvin

and indicate that J has a value of 4500°K for polyethylene membranes.

Temperature effects of the DO membrane are eliminated by multiplying equation B-7 by

$$B_1 e^{\frac{B_2}{T}} \qquad (B-8)$$

and setting the magnitudes of B_2 and J equal.

This form of compensation is inherent in most DO parametric systems.

Data consistent with Briggs and Viney[B-10] were also obtained by the authors on EPA contracts.[B-11] Comparable data were obtained for the Honeywell sensor with and without temperature compensation.

In samples having relatively high salt content, DO determinations by the Winkler process indicate a lower value than that obtained from the sensor. Mancy[B-12] notes that current due to reduced oxygen is an exponential function of ionic strength, AI, of the sample:

$$i = ACe^{K_s \Delta I} \qquad (B\text{-}9)$$

where i = sensitivity at a reference state, amperes per mg/l DO

C = DO concentration, mg/l

K_s = salting out coefficient

ΔI = ionic strength

The ionic strength is defined as:[B-13]

$$I = \frac{1}{2} \sum^{i} m_i Z_i^2$$

where m_i = molar concentration of ions

Z_i = ionic charge

To reduce the oxygen current, i, to direct proportionality in AC and thereby eliminate the salting out effects, it is evident that an equivalent multiplier of

$$B_0 e^{-K_s \Delta I}$$

be generated. This can be developed by a special conductance parametric system (Mancy[B-12] notes that there is a linear relationship

between conductance and ionic strength under selected conditions) and analog multiplication module. The Honeywell system investigated was not provided with salt compensation.

The philosophy of instrumental DO measurements is to approximate[2] Winkler determinations (as accurately as practical under selected conditions). Temperature compensation has, therefore, become an integral component of field measurement systems. Compensation for salinity is more sophisticated and costly, and its use has been avoided. In offshore oceanographic applications unaffected by estuaries, the conductivity is reasonably constant, and salinity effects on the DO concentration can be corrected by periodic field calibration.

Depending on the DO measurement tolerances, salinity correction may be necessary in estuarial studies, or in expanded monitoring programs involving selected industrial discharges. In these operations, compensation can be effected by: (1) periodic, manual instrument recalibration; (2) automatic compensation.

Since the conductivity could be reasonably predicted for estuarial studies (or actually measured by a conductance instrument along with the DO measurement) either manual or automatic correction at the data processing center could be employed. Thus, salinity compensation in this application is a convenience, but manpower (for frequent calibration checks) may not be available.

Saline discharges from selected industries may not be as predictable as tidal effects, therefore automatic compensation has merit.

Mancy has provided an instrumental method for temperature and salinity compensation for DO measurement.[B-5] His circuit first compensates sensor output for a change in salinity and lastly for a change in temperature. It should be noted that both membrane permeability and conductance are temperature dependent.

Table B-1 summarizes the levels of saturated DO as a function of temperature and chlorides.

[2]It is well known to the laboratory chemist that in some instances the Winkler determination must be modified to accurately determine the DO concentration--hence, the chemical components of the water sample must be known. All DO parametric systems are, however, calibrated in accordance with the Winkler determination.

Table B-1. SATURATED DO FOR SELECTED VALUES OF TEMPERATURE AND CHLORIDES*

Temperature C	0	Chloride concentration - mg/l 5,000	10,000	15,000	20,000
		Dissolved oxygen - mg/l			
0	14.6	13.8	13.0	12.1	11.3
5	12.8	12.1	11.4	10.7	10.0
10	11.3	10.7	10.1	9.6	9.0
15	10.2	9.7	9.1	8.6	8.1
20	9.2	8.7	8.3	7.9	7.4
25	8.4	8.0	7.6	7.2	6.7
30	7.6	7.3	6.9	6.5	6.1
35	7.1	***	***	***	***

*From Standard Methods, 13th Edition, Pages 480-481.

APPENDIX B

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